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**(54) Title:** POLYURETHANES AND PROCESSES FOR PREPARING SAME

**(57) Abstract**

This invention relates to polyurethanes of various types prepared from certain substituted hydrocarbon diols and/or derivatives of said substituted hydrocarbon diols, and polyfunctional isocyanates. The polyurethanes are useful in preparing coatings, inks, adhesives, sealants, elastomers, and foams. In particular, the invention relates to polyurethanes cured by means of moisture, blocked amines, or related compounds.

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# POLYURETHANES AND PROCESSES FOR PREPARING SAME

## Brief Summary of the Invention

### Technical Field

This invention relates to polyurethanes of various types prepared from certain substituted hydrocarbon diols and/or derivatives of said substituted hydrocarbon diols, and polyfunctional isocyanates. The polyurethanes are useful in preparing coatings, inks, adhesives, sealants, elastomers, and foams. In particular, the invention relates to polyurethanes cured by means of moisture, blocked amines, or related compounds.

### Background of the Invention

Polyurethanes are well known articles of commerce and are marketed in various forms illustrative of which are coatings, sealants, foams, elastomers, and the like. Room temperature curable or cold hardening polyurethanes are known compounds that are commercially sold and used. Such polyurethanes change from the liquid to solid state and harden by reacting and/or crosslinking an isocyanate prepolymer, which is a polymeric material that has free isocyanate groups, with water, usually available as moisture in ambient air. The reaction of water with an isocyanate results in the release of carbon dioxide and the formation of urea groups.

A second method of hardening the coating is to use capped or blocked chain extenders. When the chain extender is heated, the capping or protecting group is cleaved and the chain extender, most often an amine, reacts with the free isocyanate groups and cures the coating. In this latter method the reaction proceeds at a faster rate than in the former method, since the carbon dioxide formation and elimination step is negated and the highly reactive

amine is directly formed when the capped molecule is cleaved with moisture.

Other types of polyurethanes include two-package systems in which isocyanate-terminated polyols form adducts and one of the packages and polyols/glycols form the second package of a coating, ink, adhesive or sealant; elastomers which can be used in a molded product or solution coating manner; foams of both a rigid and a flexible nature which are used as cushioning, as insulation, as packaging materials, as oil adsorbants etc.; reaction injection molded plastic parts that are used in the automotive, building, and other industries; and similar products.

Physical characteristics of the polyurethanes and resulting products are affected by the polyol used to make the polyurethane, the polyfunctional isocyanate used, the average functionality of the polyol and the isocyanate, and the ratio of difunctional to trifunctional or higher functionality polyol used in preparing the polyurethane, and the means used to cure or crosslink the polyurethane when such a mechanism is employed. Cure rate can be enhanced by use of small amounts of a catalyst such as dibutyltin dilaurate, stannous octanoate, zinc octanoate and similar organometallic compounds.

The polyurethane products are useful in a variety of ways. Moisture-curable polyurethanes are used in varnishes of various types, including those used in finishing woodwork and doors in homes and industrial building, athletic surfaces, and in similar ways. Illustrative of other end uses for various polyurethane products include coatings for concrete, fabrics, golf balls, seamless flooring, and leather; cast and molded products; elastomers; fibers; foams; and the like.

Although the known moisture curing polyurethanes have many uses, they also have shortcomings among which are moisture and chemical resistance. Such attack can lead to failure in a functional and/or a decorative sense. An improvement in these

properties is highly desirable since it would result in longer usable lifetimes of the coated material, savings in energy and labor resources by decreasing the need for repair, and with fewer times of repair be ecologically sound because less total coating would be required over the lifetime of use and it would increase the time before replacement is required.

Moisture-curable polyurethanes are well-known articles of commerce and are described in ASTM D 16 as Type II, one-package moisture cured products that are urethane coatings characterized as having free isocyanate groups and capable of conversion to useful films by reaction of the free isocyanate groups with adventitious or other water usually in the form of moisture. Also included in the purvey of this invention are those polyurethanes that are described in ASTM D 16 as Type III, one-package heat cured products that are urethane coatings that dry or cure by thermal release of blocking agents which results in the regeneration of active isocyanate groups that afterward cure with substance containing active hydrogen groups including adventitious or other water. Other useful polyurethanes include two-package catalyzed polyurethanes (ASTM Type IV) wherein one package contains a prepolymer or adduct having free isocyanate groups capable of forming useful films by combining with a relatively small quantity of catalyst, accelerator, or crosslinking agent such as a polyol or polyamine contained in a second package; two-package polyol polyurethanes (ASTM Type V) which comprise systems wherein one package contains a prepolymer or adduct or other polyisocyanate capable of forming useful films by combining with a substantial quantity of a second package containing a resin having active hydrogen groups with or without use of a catalyst; and one-package nonreactive lacquer polyurethanes (ASTM Type VI) characterized by the absence of any significant quantity of free isocyanate or other functional groups and convert to solids primarily by solvent evaporation.

Disclosure of the Invention

It has been found that polyurethanes, particularly moisture-curable polyurethanes, can be prepared from certain substituted hydrocarbon diols and/or derivatives of said substituted hydrocarbon diols, polyfunctional isocyanates, and optionally other polyols. The substituted hydrocarbon diols are comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms.

This invention also relates to a process for preparing polyurethanes which comprises reacting a substituted hydrocarbon diol comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms, and/or a derivative of said substituted hydrocarbon diol, with a polyfunctional isocyanate and optionally other polyols to form said polyurethane.

The preferred polyurethanes are comprised of isocyanate-terminated species that are prepared from two moles of diisocyanate and one mole of a substituted hydrocarbon diol.

Polyurethanes of this type are useful in a variety of ways illustrative of which are moisture-curable polyurethanes that are useful as coatings, inks, sealants, and adhesives; prepolymers that may be reacted with polyols, polyamines or polyimines that can be made into relatively high or high molecular polyurethanes or polyurethane/ureas that are useful as elastomers, foams, fibers, molded parts from reaction injection molding and other techniques;

alcohols, amines, imines, alkanolamines, to produce a variety of products useful in their own right as chemical intermediates, solvents, medical implants, pharmaceuticals, pharmaceutical intermediates; herbicides, biocides, dye intermediates, stabilizers, antioxidants, fungicides for photographic gelatins, textile chemicals, oil absorbents and the like.

## Detailed Description

It has been discovered that polyurethanes, particularly moisture-curable polyurethanes (ASTM Type II) and thermally-curable blocked polyurethanes (ASTM Type III), can be prepared by reacting substituted hydrocarbon diols comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms, and/or derivatives of said substituted hydrocarbon diols, multifunctional isocyanates, and optionally other polyols to form isocyanate-terminated products that are useful as intermediates that can be cured by means of adventitious water usually supplied in the form of atmospheric moisture, of supplied moisture, by thermal means, or by a combination of thermal means and moisture obtained in an adventitious or supplied manner.

Other polyurethanes that fall within the purvey of this invention include the ASTM Type IV two-package catalyzed polyurethanes wherein one package contains a prepolymer or adduct having free isocyanate groups capable of forming useful films by combining with a relatively small quantity of catalyst, accelerator, or crosslinking agent such as a polyol or polyamine contained in a second package; ASTM Type V two-package polyol polyurethanes which comprise systems wherein one package contains a prepolymer or adduct or other polyisocyanate capable of forming useful films by

combining with a substantial quantity of a second package containing a resin having active hydrogen groups with or without use of a catalyst; and ASTM Type VI one-package nonreactive lacquer polyurethanes characterized by the absence of any significant quantity of free isocyanate or other functional groups and convert to solids primarily by solvent evaporation.

The substituted hydrocarbon diols useful in this invention can be represented by the formula:

$$HO-R'^{1}-OH \qquad (I)$$

wherein $R'^1$ is a substituted hydrocarbon residue having 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms.

Preferred substituted hydrocarbon diols useful in this invention include substituted 1,3-propanediols represented by the formula:

$$HOCH_2-\underset{R'^3}{\overset{R'^2}{\underset{|}{\overset{|}{C}}}}-CH_2OH \qquad (II)$$

wherein $R'^2$ and $R'^3$ are the same or different and are linear or branched alkyl having from 1 to 4 carbon atoms.

The hydrocarbon diols useful in this invention do not include liquid hydrocarbon diols that are comprised of primary

hydroxyl groups and 8 or more carbon atoms in which the primary hydroxyl groups are separated by 4 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms, said liquid hydrocarbon diol existing as a liquid at a temperature of 35°C or less.

The substituted hydrocarbon diols useful in this invention can be prepared by a process which comprises subjecting a first reaction mixture comprising a substituted hydroxyaldehyde to hydrogenation in the presence of a hydrogenation catalyst to produce a second reaction mixture comprising said substituted hydrocarbon diol.

The substituted hydrocarbon diols useful in this invention can also be prepared by a process which comprises: (1) subjecting a first reaction mixture comprising a substituted first aldehyde and a substituted or unsubstituted second aldehyde to aldol condensation in the presence of an aldol condensation catalyst to produce a second reaction mixture comprising a substituted hydroxyaldehyde; and (2) subjecting said second reaction mixture to hydrogenation in the presence of a hydrogenation catalyst to produce a third reaction mixture comprising said substituted hydrocarbon diol.

The substituted hydrocarbon diols useful in this invention can further be prepared by a process which comprises: (1) reacting an olefinically unsaturated compound with carbon monoxide and hydrogen in the presence of a metal-ligand complex catalyst to produce a first reaction mixture comprising a substituted first aldehyde; (2) subjecting said first reaction mixture and a substituted or unsubstituted second aldehyde to aldol condensation in the presence of an aldol condensation catalyst to produce a second reaction mixture comprising a substituted hydroxyaldehyde; and (3) subjecting said second reaction mixture to hydrogenation in the presence of a hydrogenation catalyst to produce a third reaction mixture comprising said substituted hydrocarbon diol.

Hydroformylation Step

The hydroformylation reaction may be asymmetric or non-asymmetric, the preferred processes being non-asymmetric, and may be conducted in any continuous or semi-continuous fashion and may involve any catalyst liquid and/or gas recycle operation desired. Thus it should be clear that the particular hydroformylation process for producing such aldehydes from an olefinic unsaturated compound, as well as the reaction conditions and ingredients of the hydroformylation process are not critical features of this invention. As used herein, the term "hydroformylation" is contemplated to include, but not limited to, all permissible asymmetric and non-asymmetric hydroformylation processes which involve converting one or more substituted or unsubstituted olefinic compounds or a reaction mixture comprising one or more substituted or unsubstituted olefinic compounds to one or more substituted or unsubstituted aldehydes or a reaction mixture comprising one or more substituted or unsubstituted aldehydes.

Illustrative metal-organophosphorus ligand complex catalyzed hydroformylation processes include such processes as described, for example, in U.S. Patent Nos. 4,148,830; 4,593,127; 4,769,498; 4,717,775; 4,774,361; 4,885,401; 5,264,616; 5,288,918; 5,360,938; 5,364,950; and 5,491,266; the disclosures of which are incorporated herein by reference. Accordingly, the hydroformylation processing techniques of this invention may correspond to any known processing techniques. Preferred processes are those involving catalyst liquid recycle hydroformylation processes.

In general, such catalyst liquid recycle hydroformylation processes involve the production of aldehydes by reacting an olefinic unsaturated compound with carbon monoxide and hydrogen in the presence of a metal-organophosphorus ligand complex catalyst in a liquid medium that also contains an organic solvent for the catalyst

and ligand. Preferably free organophosphorus ligand is also present in the liquid hydroformylation reaction medium. By "free organophosphorus ligand" is meant organophosphorus ligand that is not complexed with (tied to or bound to) the metal, e.g., metal atom, of the complex catalyst. The recycle procedure generally involves withdrawing a portion of the liquid reaction medium containing the catalyst and aldehyde product from the hydroformylation reactor (i.e., reaction zone), either continuously or intermittently, and recovering the aldehyde product therefrom by use of a composite membrane such as disclosed in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5, 1995, the disclosures of which are incorporated herein by reference, or by the more conventional and preferred method of distilling it (i.e., vaporization separation) in one or more stages under normal, reduced or elevated pressure, as appropriate, in a separate distillation zone, the non-volatilized metal catalyst containing residue being recycled to the reaction zone as disclosed, for example, in U.S. Patent No. 5,288,918. Condensation of the volatilized materials, and separation and further recovery thereof, for example, by further distillation, can be carried out in any conventional manner, the crude aldehyde product can be passed on for further purification and isomer separation, if desired, and any recovered reactants, e.g., olefinic starting material and syn gas, can be recycled in any desired manner to the hydroformylation zone (reactor). The recovered metal catalyst containing raffinate of such membrane separation or recovered non-volatilized metal catalyst containing residue of such vaporization separation can be recycled, to the hydroformylation zone (reactor) in any conventional manner desired.

In a preferred embodiment, the hydroformylation reaction mixtures employable herein includes any organic solution derived from any corresponding hydroformylation process that contains at least some amount of four different main ingredients or components, i.e., the aldehyde product, a metal-organophosphorus ligand complex catalyst,

free organophosphorus ligand and an organic solubilizing agent for said catalyst and said free ligand, said ingredients corresponding to those employed and/or produced by the hydroformylation process from whence the hydroformylation reaction mixture starting material may be derived. It is to be understood that the hydroformylation reaction mixture compositions employable herein can and normally will contain minor amounts of additional ingredients such as those which have either been deliberately employed in the hydroformylation process or formed in situ during said process. Examples of such ingredients that can also be present include unreacted olefin starting material, carbon monoxide and hydrogen gases, and in situ formed type products, such as saturated hydrocarbons and/or unreacted isomerized olefins corresponding to the olefin starting materials, and high boiling liquid aldehyde condensation byproducts, as well as other inert co-solvent type materials or hydrocarbon additives, if employed.

Illustrative metal-organophosphorus ligand complex catalysts employable in such hydroformylation reactions encompassed by this invention are known in the art and include those disclosed in the above mentioned patents. In general such catalysts may be preformed or formed in situ as described in such references and consist essentially of metal in complex combination with an organophosphorus ligand. It is believed that carbon monoxide is also present and complexed with the metal in the active species. The active species may also contain hydrogen directly bonded to the metal.

The catalyst useful in the hydroformylation reaction includes a metal-organophosphorus ligand complex catalyst which can be optically active or non-optically active. The permissible metals which make up the metal-organophosphorus ligand complexes include Group 8, 9 and 10 metals selected from rhodium (Rh), cobalt (Co), iridium (Ir), ruthenium (Ru), iron (Fe), nickel (Ni), palladium (Pd), platinum (Pt), osmium (Os) and mixtures thereof, with the preferred metals being rhodium, cobalt, iridium and ruthenium, more preferably

rhodium, cobalt and ruthenium, especially rhodium. Other permissible metals include Group 11 metals selected from copper (Cu), silver (Ag), gold (Au) and mixtures thereof, and also Group 6 metals selected from chromium (Cr), molybdenum (Mo), tungsten (W) and mixtures thereof. Mixtures of metals from Groups 6, 8, 9, 10 and 11 may also be used in this invention. The permissible organophosphorus ligands which make up the metal-organophosphorus ligand complexes include organophosphines, e.g., triorganophosphines, and organophosphites, e.g., mono-, di-, tri- and polyorganophosphites. Other permissible organophosphorus ligands include, for example, organophosphonites, organophosphinites, organophosphorus amides and the like. Mixtures of such ligands may be employed if desired in the metal-ligand complex catalyst and/or free ligand and such mixtures may be the same or different. This invention is not intended to be limited in any manner by the permissible organophosphorus ligands or mixtures thereof. It is to be noted that the successful practice of this invention does not depend and is not predicated on the exact structure of the metal-ligand complex species, which may be present in their mononuclear, dinuclear and/or higher nuclearity forms. Indeed, the exact structure is not known. Although it is not intended herein to be bound to any theory or mechanistic discourse, it appears that the catalytic species may in its simplest form consist essentially of the metal in complex combination with the ligand and carbon monoxide when used.

The term "complex" as used herein and in the claims means a coordination compound formed by the union of one or more electronically rich molecules or atoms capable of independent existence with one or more electronically poor molecules or atoms, each of which is also capable of independent existence. For example, the organophosphorus ligands employable herein may possess one or more phosphorus donor atoms, each having one available or unshared pair of electrons which are each capable of forming a coordinate covalent bond

independently or possibly in concert (e.g., via chelation) with the metal. Carbon monoxide (which is also properly classified as a ligand) can also be present and complexed with the metal. The ultimate composition of the complex catalyst may also contain an additional ligand, for example, hydrogen or an anion satisfying the coordination sites or nuclear charge of the metal. Illustrative additional ligands include, for example, halogen (Cl, Br, I), alkyl, aryl, substituted aryl, acyl, $CF_3$, $C_2F_5$, CN, $(R)_2PO$ and RP(O)(OH)O (wherein each R is the same or different and is a substituted or unsubstituted hydrocarbon radical, e.g., the alkyl or aryl), acetate, acetylacetonate, $SO_4$, $PF_4$, $PF_6$, $NO_2$, $NO_3$, $CH_3O$, $CH_2{=}CHCH_2$, $CH_3CH{=}CHCH_2$, $C_6H_5CN$, $CH_3CN$, NO, $NH_3$, pyridine, $(C_2H_5)_3N$, mono-olefins, diolefins and triolefins, tetrahydrofuran, and the like. It is of course to be understood that the complex species are preferably free of any additional organic ligand or anion that might poison the catalyst and have an undue adverse effect on catalyst performance. It is preferred in the metal-organophosphorus ligand complex catalyzed hydroformylation reactions that the active catalysts be free of halogen and sulfur directly bonded to the metal, although such may not be absolutely necessary. Preferred metal-ligand complex catalysts include rhodium-organophosphine ligand complex catalysts and rhodium-organophosphite ligand complex catalysts.

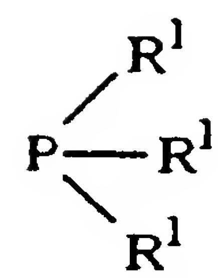
The number of available coordination sites on such metals is well known in the art. Thus the catalytic species may comprise a complex catalyst mixture, in their monomeric, dimeric or higher nuclearity forms, which are preferably characterized by at least one organophosphorus-containing molecule complexed per one molecule of metal, e.g., rhodium. As noted above, it is considered that the catalytic species of the preferred catalyst employed in the hydroformylation reaction may be complexed with carbon monoxide and hydrogen in addition to the organophosphorus ligands in view of the carbon

monoxide and hydrogen gas employed by the hydroformylation reaction.

The organophosphines and organophosphites that may serve as the ligand of the metal-organophosphorus ligand complex catalyst and/or free ligand of the hydroformylation reaction may be of the achiral (optically inactive) or chiral (optically active) type and are well known in the art. Achiral organophosphorus ligands are preferred.

Among the organophosphines that may serve as the ligand of the metal-organophosphine complex catalyst and/or free organophosphine ligand of the hydroformylation reaction mixture starting materials are triorganophosphines, trialkylphosphines, alkyldiarylphosphines, dialkylarylphosphines, dicycloalkylarylphosphines, cycloalkyldiarylphosphines, triaralkylphosphines, tricycloalkylphosphines, and triarylphosphines, alkyl and/or aryl biphosphines and bisphosphine mono oxides, as well as ionic triorganophosphines containing at least one ionic moiety selected from the salts of sulfonic acid, of carboxylic acid, of phosphonic acid and of quaternary ammonium compounds, and the like. Of course any of the hydrocarbon radicals of such tertiary non-ionic and ionic organophosphines may be substituted if desired, with any suitable substituent that does not unduly adversely affect the desired result of the hydroformylation reaction. The organophosphine ligands employable in the hydroformylation reaction and/or methods for their preparation are known in the art.

Illustrative triorganophosphine ligands may be represented by the formula:



(III)

wherein each $R^1$ is the same or different and is a substituted or unsubstituted monovalent hydrocarbon radical, e.g., an alkyl or aryl radical. Suitable hydrocarbon radicals may contain from 1 to 24 carbon atoms or greater, the most preferred hydrocarbon radical being phenyl, ($C_6H_5$—). Illustrative substituent groups that may be present on the aryl radicals include, e.g., alkyl radicals, alkoxy radicals, silyl radicals such as —$Si(R^2)_3$; amino radicals such as —$N(R^2)_2$; acyl radicals such as —$C(O)R^2$; carboxy radicals such as —$C(O)OR^2$; acyloxy radicals such as —$OC(O)R^2$; amido radicals such as —$C(O)N(R^2)_2$ and —$N(R^2)C(O)R^2$; ionic radicals such as —$SO_3M$ wherein M represents inorganic or organic cation; sulfonyl radicals such as —$SO_2R^2$; ether radicals such as —$OR^2$; sulfinyl radicals such as —$SOR^2$; sulfenyl radicals such as —$SR^2$ as well as halogen, nitro, cyano, trifluoromethyl and hydroxy radicals, and the like, wherein each $R^2$ individually represents the same or different substituted or unsubstituted monovalent hydrocarbon radical, with the proviso that in amino substituents such as —$N(R^2)_2$, each $R^2$ taken together can also represent a divalent bridging group that forms a heterocyclic radical with the nitrogen atom and in amido substituents such as $C(O)N(R^2)_2$ and —$N(R^2)C(O)R^2$ each —$R^2$ bonded to N can also be hydrogen. Illustrative alkyl radicals include, e.g., methyl, ethyl, propyl, butyl and the like. Illustrative aryl radicals include, e.g., phenyl, naphthyl, diphenyl, fluorophenyl, difluorophenyl, benzoyloxyphenyl, carboethoxyphenyl, acetylphenyl, ethoxyphenyl, phenoxyphenyl, hydroxyphenyl; carboxyphenyl, trifluoromethylphenyl,

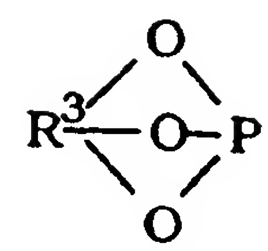
methoxyethylphenyl, acetamidophenyl, dimethylcarbamylphenyl, tolyl, xylyl, and the like.

Illustrative specific organophosphines include, e.g., triphenylphosphine, tris-p-tolyl phosphine, tris-p-methoxyphenylphosphine, tris-p-fluorophenylphosphine, tris-p-chlorophenylphosphine, tris-dimethylaminophenylphosphine, propyldiphenylphosphine, t-butyldiphenylphosphine, n-butyldiphenylphosphine, n-hexyldiphenylphosphine, cyclohexyldiphenylphosphine, dicyclohexylphenylphosphine, tricyclohexylphenylphosphine, tribenzylphosphine as well as the alkali and alkaline earth metal salts of sulfonated triphenylphosphines, e.g., of (tri-m-sulfophenyl)phosphine and of (m-sulfophenyl)diphenyl-phosphine and the like.

More particularly, illustrative metal-organophosphine complex catalysts and illustrative free organophosphine ligands include, e.g., those disclosed in U.S. Patent Nos. 3,527,809; 4,148,830; 4,247,486; 4,283,562; 4,400,548; 4,482,749 and 4,861,918, the disclosures of which are incorporated herein by reference.

Among the organophosphites that may serve as the ligand of the metal-organophosphite complex catalyst and/or free organophosphite ligand of the hydroformylation reaction mixture starting materials are monoorganophosphites, diorganophosphites, triorganophosphites and organopolyphosphites. The organophosphite ligands employable in this invention and/or methods for their preparation are known in the art.

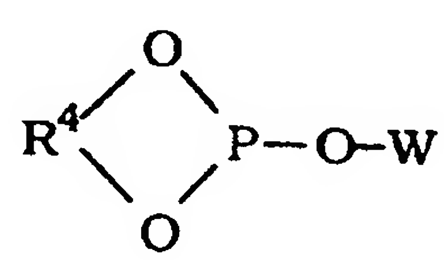
Representative monoorganophosphites may include those having the formula:



(IV)

wherein $R^3$ represents a substituted or unsubstituted trivalent hydrocarbon radical containing from 4 to 40 carbon atoms or greater, such as trivalent acyclic and trivalent cyclic radicals, e.g., trivalent alkylene radicals such as those derived from 1,2,2-trimethylolpropane and the like, or trivalent cycloalkylene radicals such as those derived from 1,3,5-trihydroxycyclohexane, and the like. Such monoorganophosphites may be found described in greater detail, for example, in U.S. Patent No. 4,567,306, the disclosure of which is incorporated herein by reference.

Representative diorganophosphites may include those having the formula:



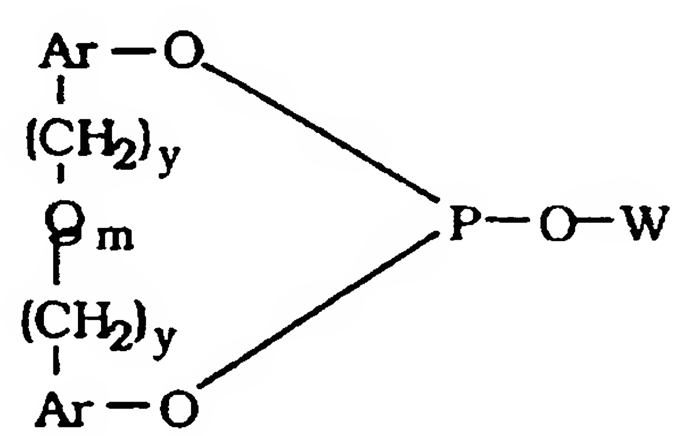
(V)

wherein $R^4$ represents a substituted or unsubstituted divalent hydrocarbon radical containing from 4 to 40 carbon atoms or greater and W represents a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 18 carbon atoms or greater.

Representative substituted and unsubstituted monovalent hydrocarbon radicals represented by W in the above formula (V) include alkyl and aryl radicals, while representative substituted and unsubstituted divalent hydrocarbon radicals represented by $R^4$ include divalent acyclic radicals and divalent

aromatic radicals. Illustrative divalent acyclic radicals include, for example, alkylene, alkylene-oxy-alkylene, alkylene-NX-alkylene wherein X is hydrogen or a substituted or unsubstituted monovalent hydrocarbon radical, alkylene-S-alkylene, and cycloalkylene radicals, and the like. The more preferred divalent acyclic radicals are the divalent alkylene radicals such as disclosed more fully, for example, in U.S. Patent Nos. 3,415,906 and 4,567,302 and the like, the disclosures of which are incorporated herein by reference. Illustrative divalent aromatic radicals include, for example, arylene, bisarylene, arylene-alkylene, arylene-alkylene-arylene, arylene-oxy-arylene, arylene-NX-arylene wherein X is as defined above, arylene-S-arylene, and arylene-S-alkylene, and the like. More preferably $R^4$ is a divalent aromatic radical such as disclosed more fully, for example, in U.S. Patent Nos. 4,599,206 and 4,717,775, and the like, the disclosures of which are incorporated herein by reference.

Representative of a more preferred class of diorganophosphites are those of the formula:

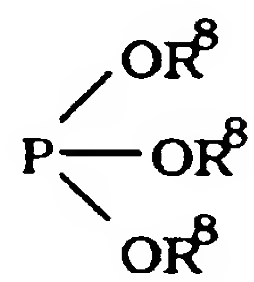



(VI)

wherein W is as defined above, each Ar is the same or different and represents a substituted or unsubstituted aryl radical, each y is the same or different and is a value of 0 or 1, Q represents a divalent bridging group selected from $-C(R^5)_2-$, -O-, -S-, $-NR^6-$, $Si(R^7)_2-$ and -CO-, wherein each $R^5$ is the same or different and represents hydrogen, alkyl radicals having from 1 to 12 carbon atoms, phenyl,

tolyl, and anisyl, $R^6$ represents hydrogen or a methyl radical, each $R^7$ is the same or different and represents hydrogen or a methyl radical, and m is a value of 0 or 1. Such diorganophosphites are described in greater detail, for example, in U.S. Patent Nos. 4,599,206, 4,717,775 and 4,835,299, the disclosures of which are incorporated herein by reference.

Representative triorganophosphites may include those having the formula:

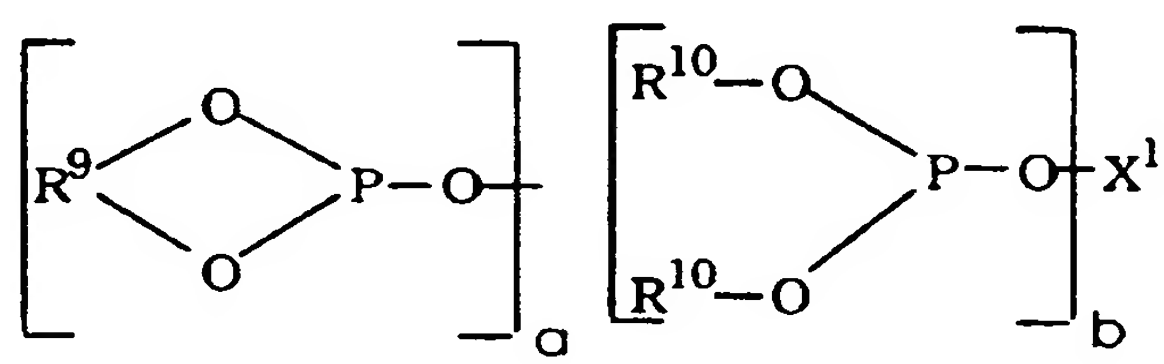


(VII)

wherein each $R^8$ is the same or different and is a substituted or unsubstituted monovalent hydrocarbon radical e.g., an alkyl, cycloalkyl, aryl, alkaryl and aralkyl radicals which may contain from 1 to 24 carbon atoms. Suitable hydrocarbon radicals may contain from 1 to 24 carbon atoms or greater and may include those described above for $R^1$ in formula (III). Illustrative triorganophosphites include, for example, trialkyl phosphites, dialkylaryl phosphites, alkyldiaryl phosphites, triaryl phosphites, and the like, such as, for example, trimethyl phosphite, triethyl phosphite, butyldiethyl phosphite, tri-n-propyl phosphite, tri-n-butyl phosphite, tri-2-ethylhexyl phosphite, tri-n-octyl phosphite, tri-n-dodecyl phosphite, dimethylphenyl phosphite, diethylphenyl phosphite, methyldiphenyl phosphite, ethyldiphenyl phosphite, triphenyl phosphite, trinaphthyl phosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)methylphosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)cyclohexylphosphite, tris(3,6-di-t-butyl-2-naphthyl)phosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)(4-biphenyl)phosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)phenylphosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)(4-

benzoylphenyl)phosphite, bis(3,6,8-tri-t-butyl-2-naphthyl)(4-sulfonylphenyl)phosphite, and the like. The most preferred triorganophosphite is triphenylphosphite. Such triorganophosphites are described in greater detail, for example, in U.S. Patent Nos. 3,527,809 and 5,277,532, the disclosures of which are incorporated herein by reference.

Representative organopolyphosphites contain two or more tertiary (trivalent) phosphorus atoms and may include those having the formula:



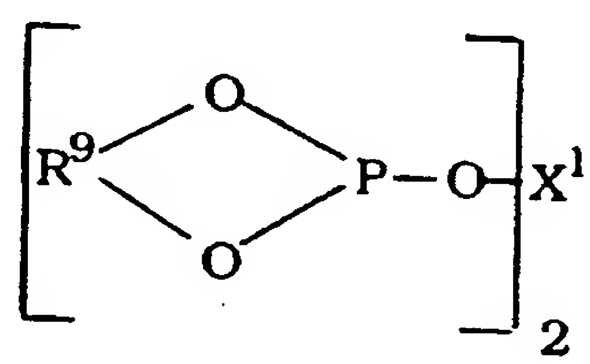
(VIII)

wherein $X^1$ represents a substituted or unsubstituted n-valent hydrocarbon bridging radical containing from 2 to 40 carbon atoms, each $R^9$ is the same or different and is a divalent hydrocarbon radical containing from 4 to 40 carbon atoms, each $R^{10}$ is the same or different and is a substituted or unsubstituted monovalent hydrocarbon radical containing from 1 to 24 carbon atoms, a and b can be the same or different and each have a value of 0 to 6, with the proviso that the sum of a + b is 2 to 6 and n equals a + b. Of course it is to be understood that when a has a value of 2 or more, each $R^9$ radical may be the same or different, and when b has a value of 1 or more, each $R^{10}$ radical may also be the same or different.

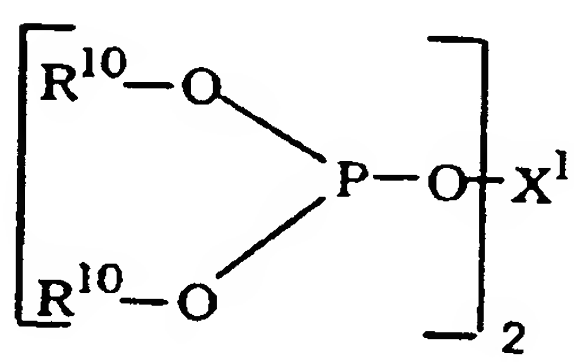
Representative n-valent (preferably divalent) hydrocarbon bridging radicals represented by $X^1$, as well as representative divalent hydrocarbon radicals represented by $R^9$ above, include both acyclic radicals and aromatic radicals, such as alkylene, alkylene-$Q_m$-alkylene, cycloalkylene, arylene, bisarylene, arylene-alkylene, and

arylene-$(CH_2)_y$-$Q_m$-$(CH_2)_y$-arylene radicals, and the like, wherein Q, m and y are as defined above for formula (VIII). The more preferred acyclic radicals represented by $X^1$ and $R^9$ above are divalent alkylene radicals, while the more preferred aromatic radicals represented by $X^1$ and $R^9$ above are divalent arylene and bisarylene radicals, such as disclosed more fully, for example, in U.S. Patent Nos. 4,769,498; 4,774,361: 4,885,401; 5,179,055; 5,113,022; 5,202,297; 5,235,113; 5,264,616 and 5,364,950, and European Patent Application Publication No. 662,468, and the like, the disclosures of which are incorporated herein by reference. Representative monovalent hydrocarbon radicals represented by each $R^{10}$ radical above include alkyl and aromatic radicals.

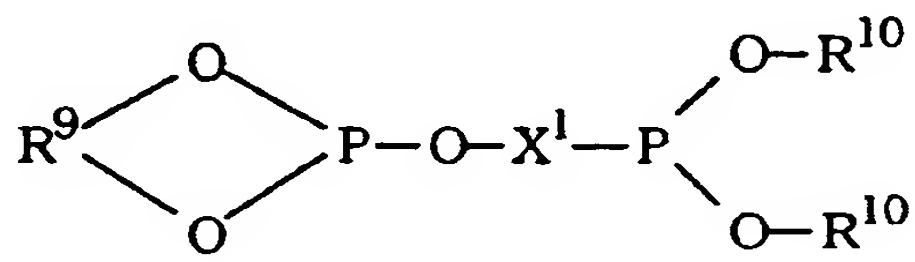
Illustrative preferred organopolyphosphites may include bisphosphites such as those of formulas (IX) to (XI) below:



(IX)



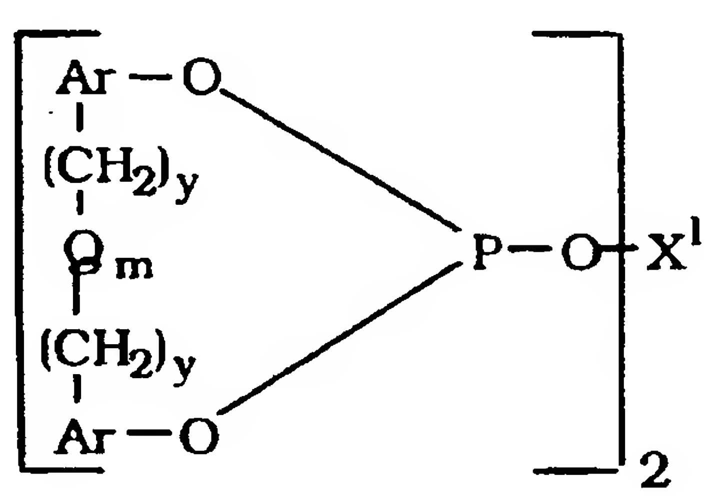
(X)



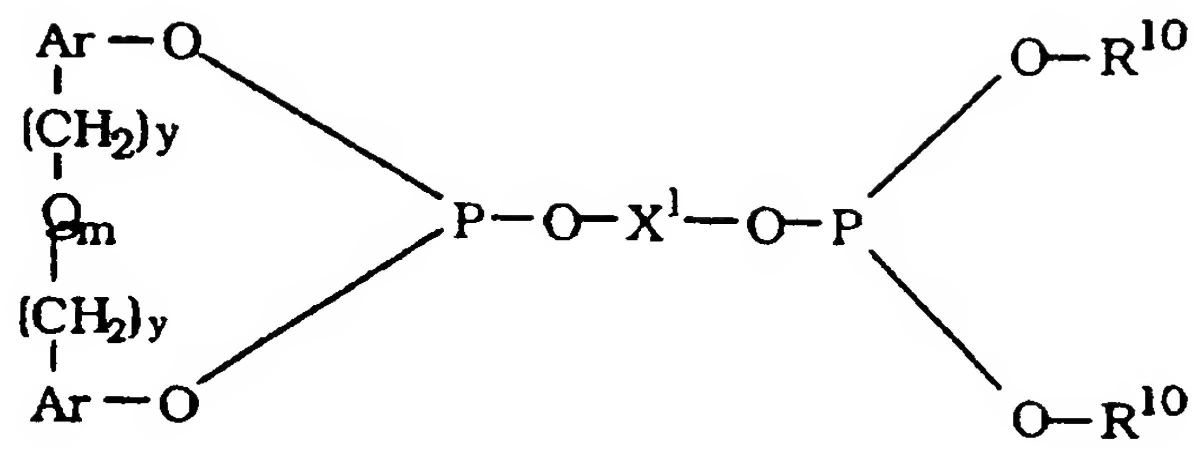
(XI)

wherein each $R^9$, $R^{10}$ and $X^1$ of formulas (IX) to (XI) are the same as defined above for formula (VIII). Preferably, each $R^9$ and $X^1$ represents a divalent hydrocarbon radical selected from alkylene, arylene, arylene-alkylene-arylene, and bisarylene, while each $R^{10}$ represents a monovalent hydrocarbon radical selected from alkyl and aryl radicals. Organophosphite ligands of such Formulas (VIII) to (XI) may be found disclosed, for example, in U.S. Patent Nos. 4,668,651; 4,748,261; 4,769,498; 4,774,361; 4,885,401; 5,113,022; 5,179,055; 5,202,297; 5,235,113; 5,254,741; 5,264,616; 5,312,996; 5,364,950; and 5,391,801; the disclosures of all of which are incorporated herein by reference.

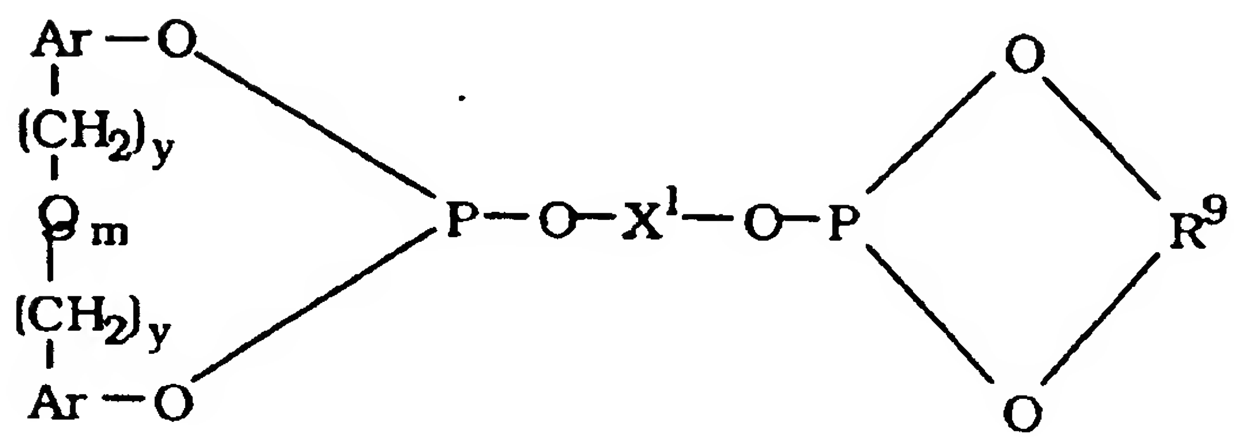
Representative of more preferred classes of organobisphosphites are those of the following formulas (XII) to (XIV):



(XII)



(XIII)



(XIV)

wherein Ar, Q , $R^9$, $R^{10}$, $X^1$, m and y are as defined above. Most preferably $X^1$ represents a divalent aryl-$(CH_2)_y$-$(Q)_m$-$(CH_2)_y$-aryl radical wherein each y individually has a value of 0 or 1; m has a value of 0 or 1 and Q is -O-, -S- or-$C(R^5)_2$- wherein each $R^5$ is the same or different and represents a hydrogen or methyl radical. More preferably each alkyl radical of the above defined $R^{10}$ groups may contain from 1 to 24 carbon atoms and each aryl radical of the above-defined Ar, $X^1$, $R^9$ and $R^{10}$ groups of the above formulas (VIII) to (XIV) may contain from 6 to 18 carbon atoms and said radicals may be the same or different, while the preferred alkylene radicals of $X^1$ may contain from 2 to 18 carbon atoms and the preferred alkylene radicals of $R^9$ may contain from 5 to 18 carbon atoms. In addition, preferably the divalent Ar radicals and divalent aryl radicals of $X^1$ of the above formulas are phenylene radicals in which the bridging group represented by –

$(CH_2)_y$–$(Q)_m$–$(CH_2)_y$– is bonded to said phenylene radicals in positions that are ortho to the oxygen atoms of the formulas that connect the phenylene radicals to their phosphorus atom of the formulae. It is also preferred that any substituent radical when present on such phenylene radicals be bonded in the para and/or ortho position of the phenylene radicals in relation to the oxygen atom that bonds the given substituted phenylene radical to its phosphorus atom.

Moreover, if desired any given organophosphite in the above formulas (IV) to (XIV) may be an ionic phosphite, i.e., may contain one or more ionic moieties selected from the group consisting of:

— $SO_3M$ wherein M represents inorganic or organic cation,

— $PO_3M$ wherein M represents inorganic or organic cation,

— $N(R^{11})_3X^2$ wherein each $R^{11}$ is the same or different and represents a hydrocarbon radical containing from 1 to 30 carbon atoms, e.g., alkyl, aryl, alkaryl, aralkyl, and cycloalkyl radicals, and $X^2$ represents inorganic or organic anion,

— $CO_2M$ wherein M represents inorganic or organic cation,

as described, for example, in U.S. Patent Nos. 5,059,710; 5,113,022 5,114,473; 5,449,653; and European Patent Application Publication No. 435,084, the disclosures of which are incorporated herein by reference. Thus, if desired, such organophosphite ligands may contain from 1 to 3 such ionic moieties, while it is preferred that only one such ionic moiety be substituted on any given aryl moiety in the organophosphite ligand when the ligand contains more than one such ionic moiety. As suitable counter-ions, M and $X^2$, for the anionic moieties of the ionic organophosphites there can be mentioned hydrogen (i.e. a proton), the cations of the alkali and alkaline earth metals, e.g., lithium, sodium, potassium, cesium, rubidium, calcium, barium, magnesium and strontium, the ammonium cation and quaternary ammonium cations, phosphonium cations, arsonium

cations and iminium cations. Suitable anionic atoms of radicals include, for example, sulfate, carbonate, phosphate, chloride, acetate, oxalate and the like.

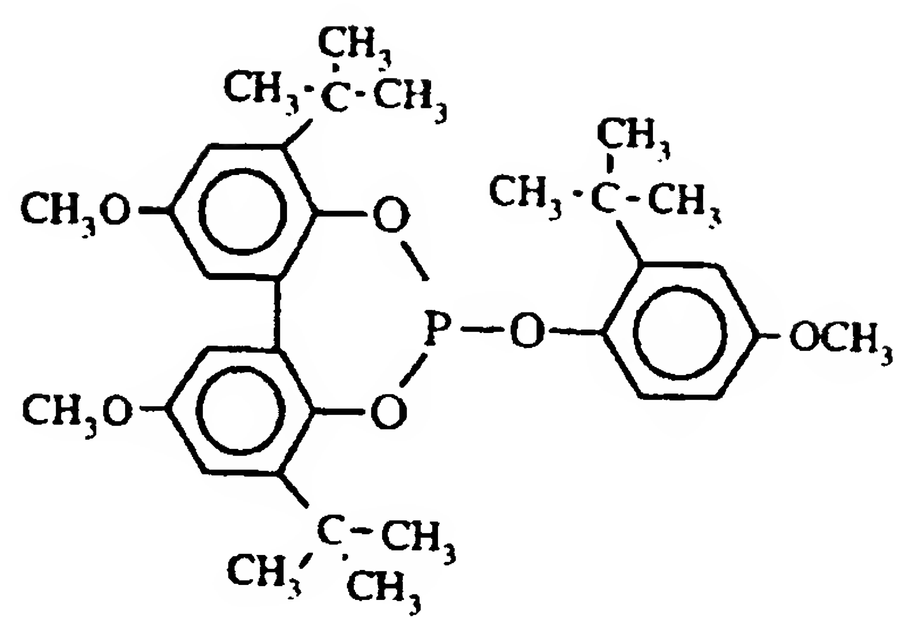
Of course any of the $R^3$, $R^4$, $R^8$, $R^9$, $R^{10}$, $X^1$, $X^2$, W, Q and Ar radicals of such non-ionic and ionic organophosphites of formulas (IV) to (XIV) above may be substituted if desired, with any suitable substituent containing from 1 to 30 carbon atoms that does not unduly adversely affect the desired result of the hydroformylation reaction. Substituents that may be on said radicals in addition of course to corresponding hydrocarbon radicals such as alkyl, aryl, aralkyl, alkaryl and cyclohexyl substituents, may include for example silyl radicals such as $-Si(R^{12})_3$; amino radicals such as $-N(R^{12})_2$; phosphine radicals such as -aryl-$P(R^{12})_2$; acyl radicals such as $-C(O)R^{12}$; acyloxy radicals such as $-OC(O)R^{12}$; amido radicals such as $-CON(R^{12})_2$ and $-N(R^{12})COR^{12}$; sulfonyl radicals such as $-SO_2R^{12}$; alkoxy radicals such as $-OR^{12}$; sulfinyl radicals such as $-SOR^{12}$; sulfenyl radicals such as $-SR^{12}$; phosphonyl radicals such as $-P(O)(R^{12})_2$; as well as, halogen, nitro, cyano, trifluoromethyl, hydroxy radicals, and the like, wherein each $R^{12}$ radical is the same or different and represents a monovalent hydrocarbon radical having from 1 to 18 carbon atoms (e.g., alkyl, aryl, aralkyl, alkaryl and cyclohexyl radicals), with the proviso that in amino substituents such as $-N(R^{12})_2$ each $R^{12}$ taken together can also represent a divalent bridging group that forms a heterocyclic radical with the nitrogen atom, and in amido substituents such as $-C(O)N(R^{12})_2$ and $-N(R^{12})COR^{12}$ each $R^{12}$ bonded to N can also be hydrogen. Of course it is to be understood that any of the substituted or unsubstituted hydrocarbon radicals groups that make up a particular given organophosphite may be the same or different.

More specifically illustrative substituents include primary, secondary and tertiary alkyl radicals such as methyl, ethyl,

n-propyl, isopropyl, butyl, sec-butyl, t-butyl, neo-pentyl, n-hexyl, amyl, sec-amyl, t-amyl, iso-octyl, decyl, octadecyl, and the like; aryl radicals such as phenyl, naphthyl and the like; aralkyl radicals such as benzyl, phenylethyl, triphenylmethyl, and the like; alkaryl radicals such as tolyl, xylyl, and the like; alicyclic radicals such as cyclopentyl, cyclohexyl, 1-methylcyclohexyl, cyclooctyl, cyclohexylethyl, and the like; alkoxy radicals such as methoxy, ethoxy, propoxy, t-butoxy, -$OCH_2CH_2OCH_3$, -$(OCH_2CH_2)_2OCH_3$, -$(OCH_2CH_2)_3OCH_3$, and the like; aryloxy radicals such as phenoxy and the like; as well as silyl radicals such as -$Si(CH_3)_3$, -$Si(OCH_3)_3$, -$Si(C_3H_7)_3$, and the like; amino radicals such as -$NH_2$, -$N(CH_3)_2$, -$NHCH_3$, -$NH(C_2H_5)$, and the like; arylphosphine radicals such as -$P(C_6H_5)_2$, and the like; acyl radicals such as -$C(O)CH_3$, -$C(O)C_2H_5$, -$C(O)C_6H_5$, and the like; carbonyloxy radicals such as -$C(O)OCH_3$ and the like; oxycarbonyl radicals such as -$O(CO)C_6H_5$, and the like; amido radicals such as -$CONH_2$, -$CON(CH_3)_2$, -$NHC(O)CH_3$, and the like; sulfonyl radicals such as -$S(O)_2C_2H_5$ and the like; sulfinyl radicals such as -$S(O)CH_3$ and the like; sulfenyl radicals such as -$SCH_3$, -$SC_2H_5$, -$SC_6H_5$, and the like; phosphonyl radicals such as -$P(O)(C_6H_5)_2$, -$P(O)(CH_3)_2$, -$P(O)(C_2H_5)_2$, -$P(O)(C_3H_7)_2$, -$P(O)(C_4H_9)_2$, -$P(O)(C_6H_{13})_2$, -$P(O)CH_3(C_6H_5)$, -$P(O)(H)(C_6H_5)$, and the like.

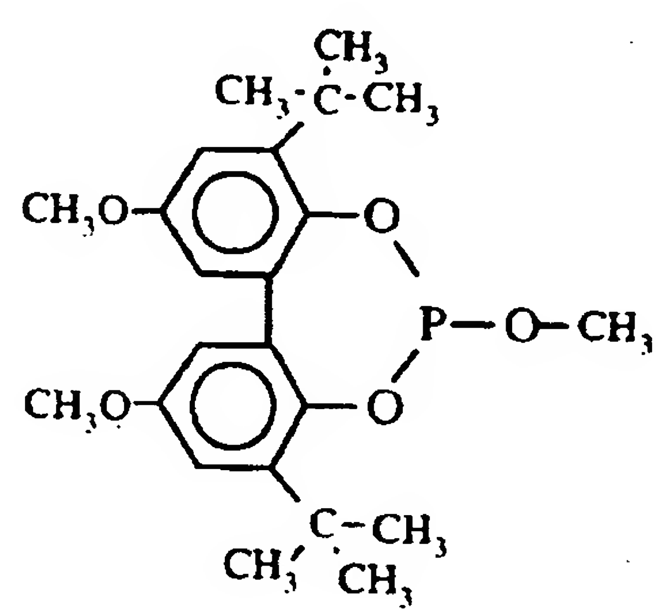
Specific illustrative examples of organophosphite ligands include the following:

2-t-butyl-4-methoxyphenyl(3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphite having the formula:



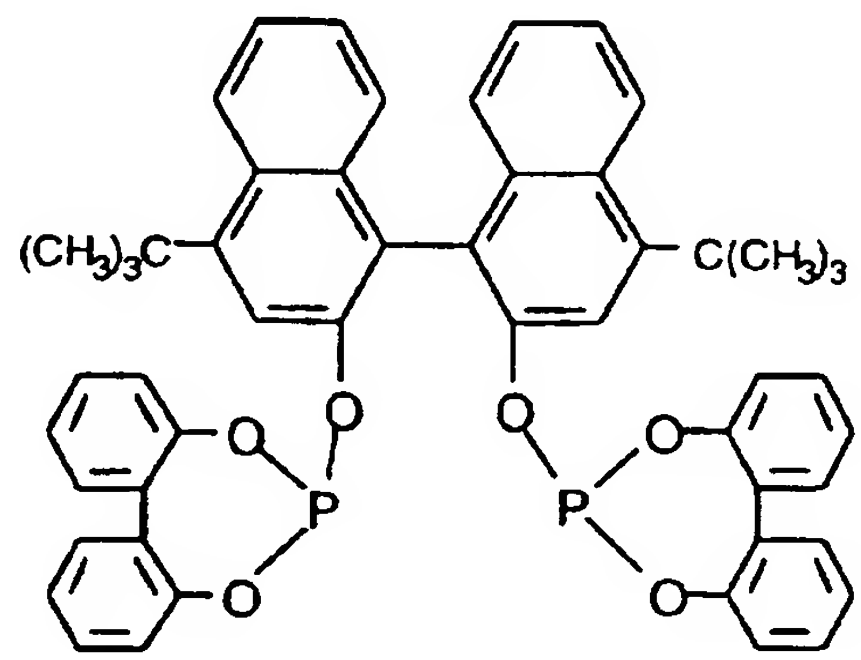
Ligand A

methyl(3,3'-di-t-butyl-5,5'-dimethoxy-1,1'-biphenyl-2,2'-diyl)phosphite having the formula:



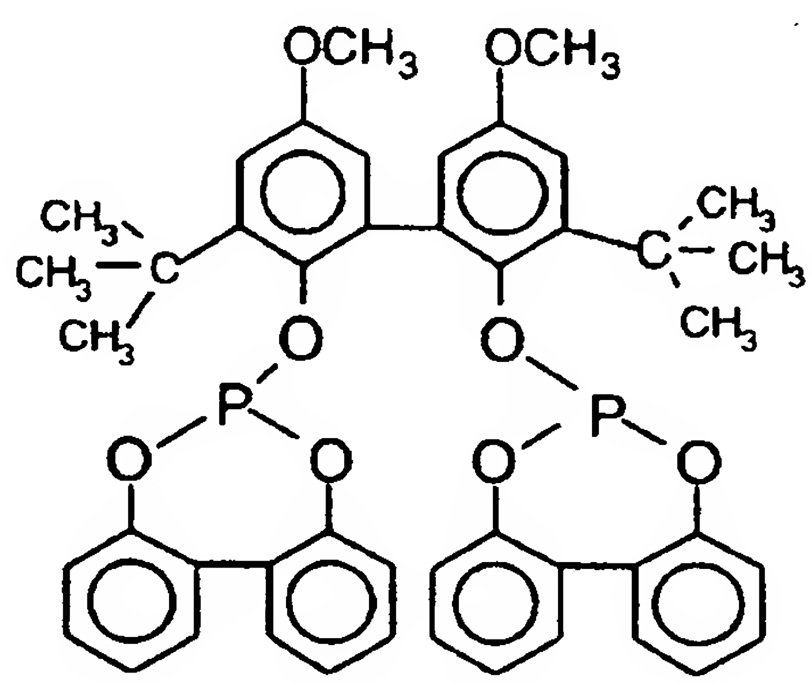
Ligand B

6,6'-[[4,4'-bis(1,1-dimethylethyl)-[1,1'-binaphthyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



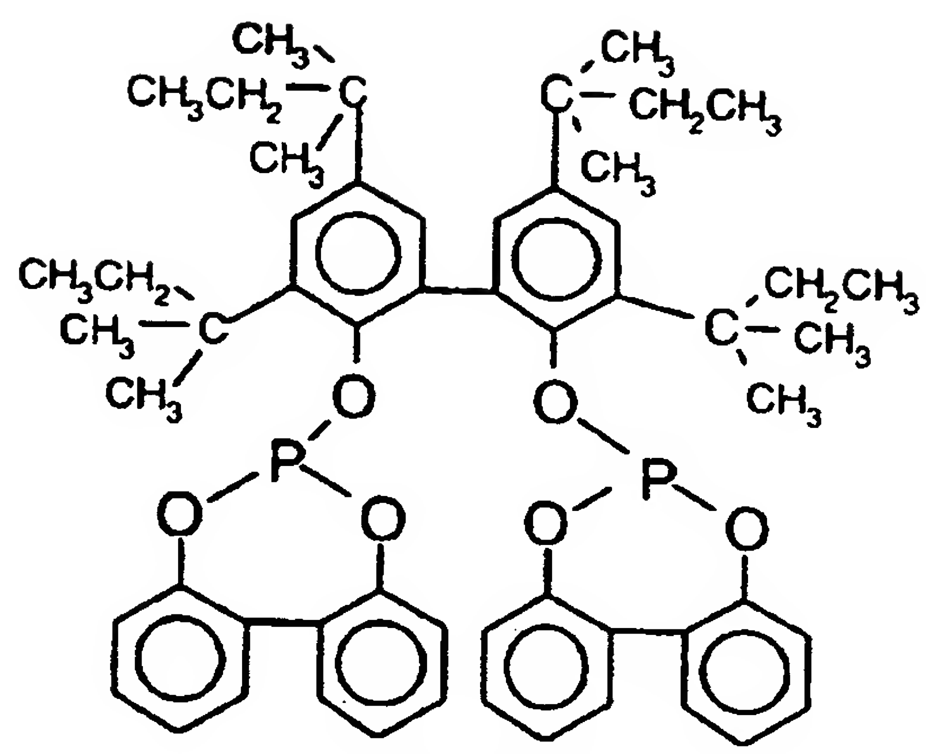

Ligand C

6,6'-[[3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



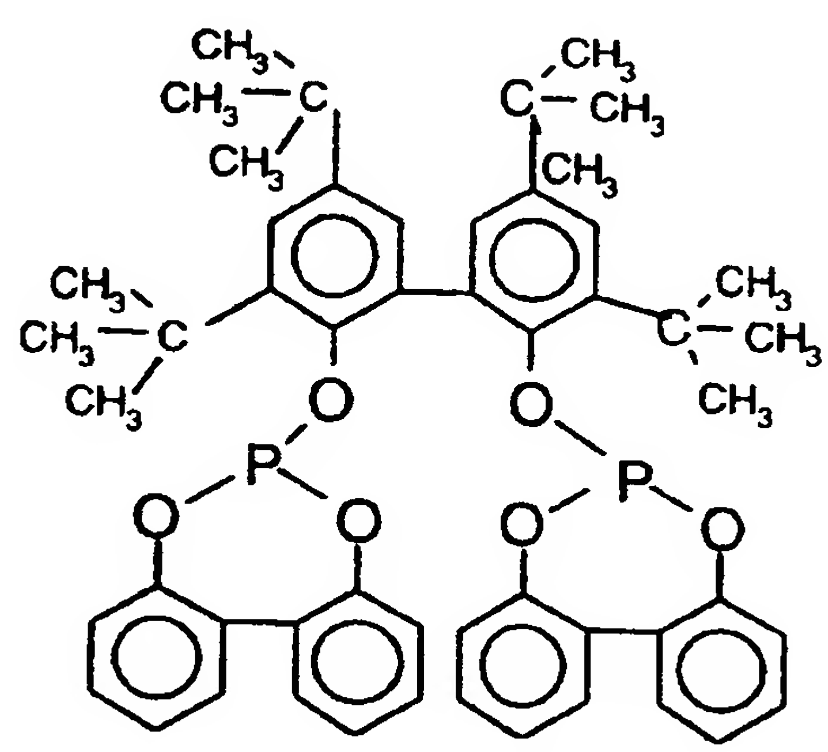

Ligand D

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylpropyl)-[1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



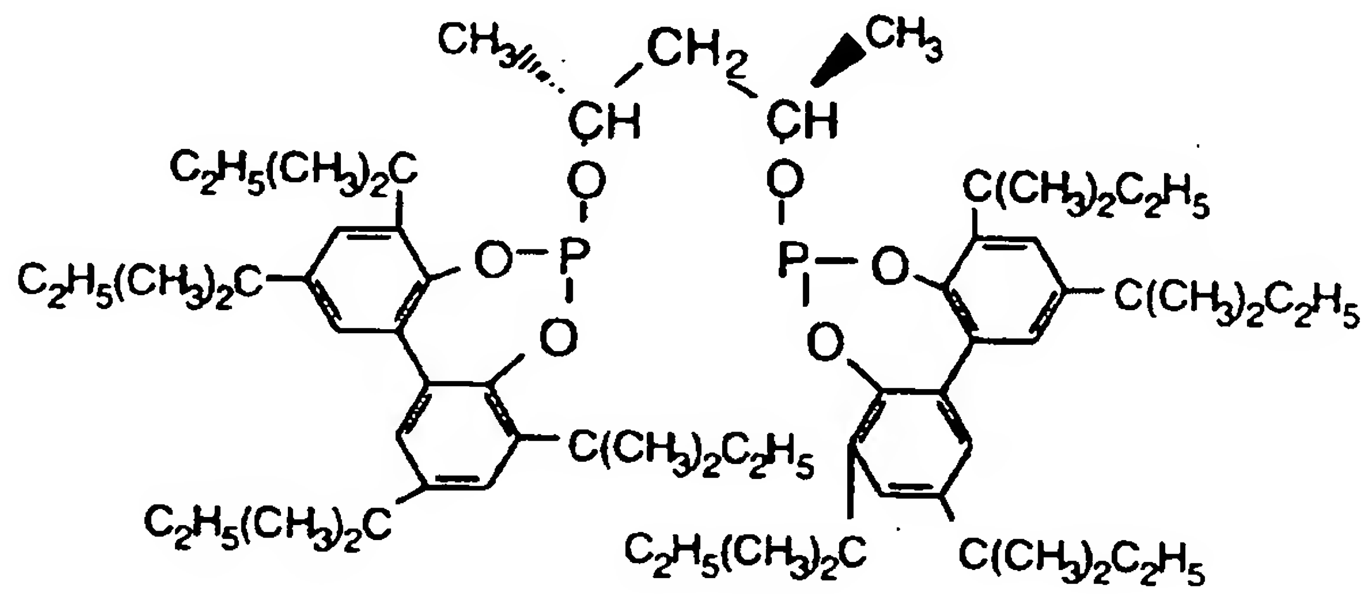
Ligand E

6,6'-[[3,3',5,5'-tetrakis(1,1-dimethylethyl)-1,1'-biphenyl]-2,2'-diyl]bis(oxy)]bis-dibenzo[d,f][1,3,2]-dioxaphosphepin having the formula:



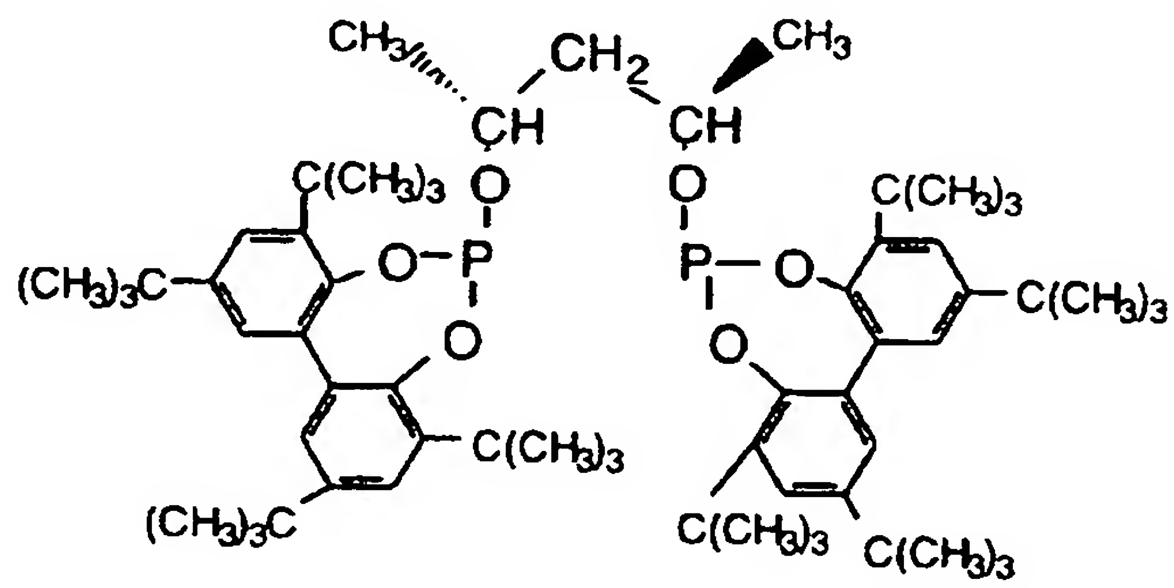
Ligand F

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-amyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



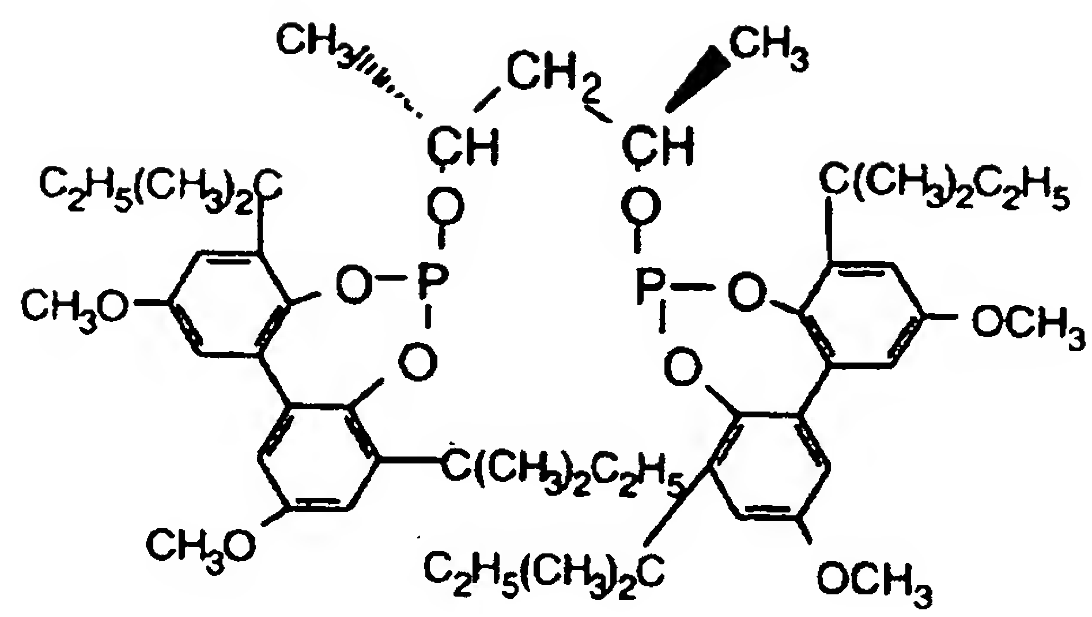
Ligand G

(2R,4R)-di[2,2'-(3,3',5,5'-tetrakis-tert-butyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



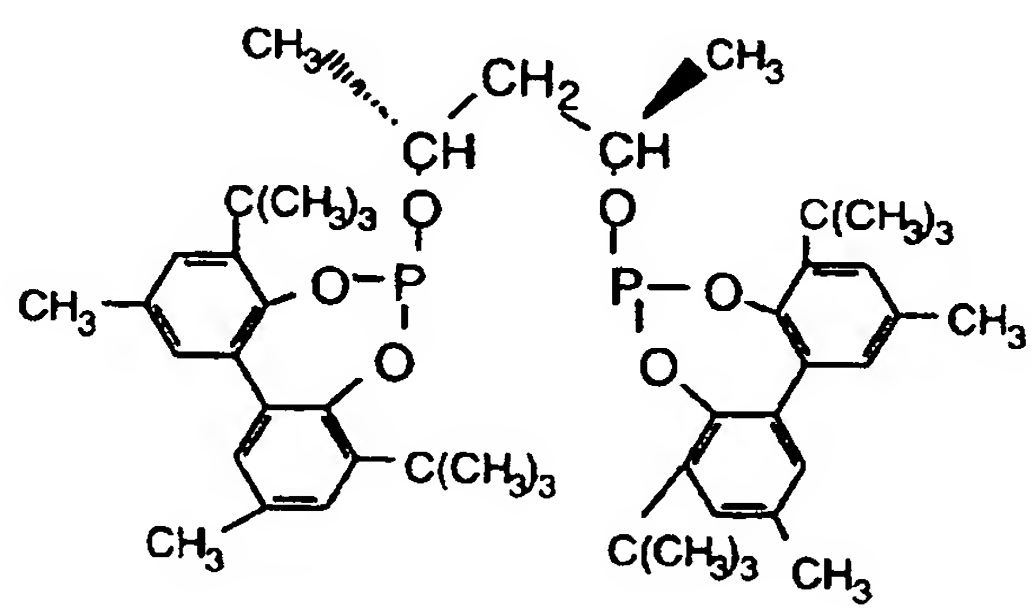
Ligand H

(2R,4R)-di[2,2'-(3,3'-di-amyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



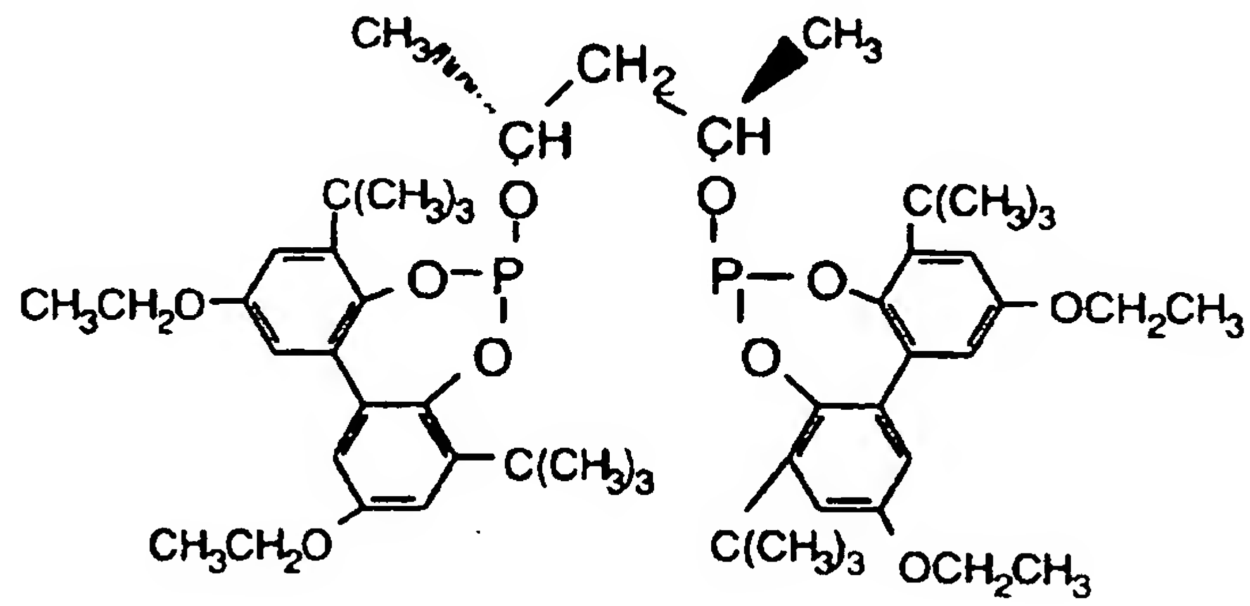
Ligand I

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



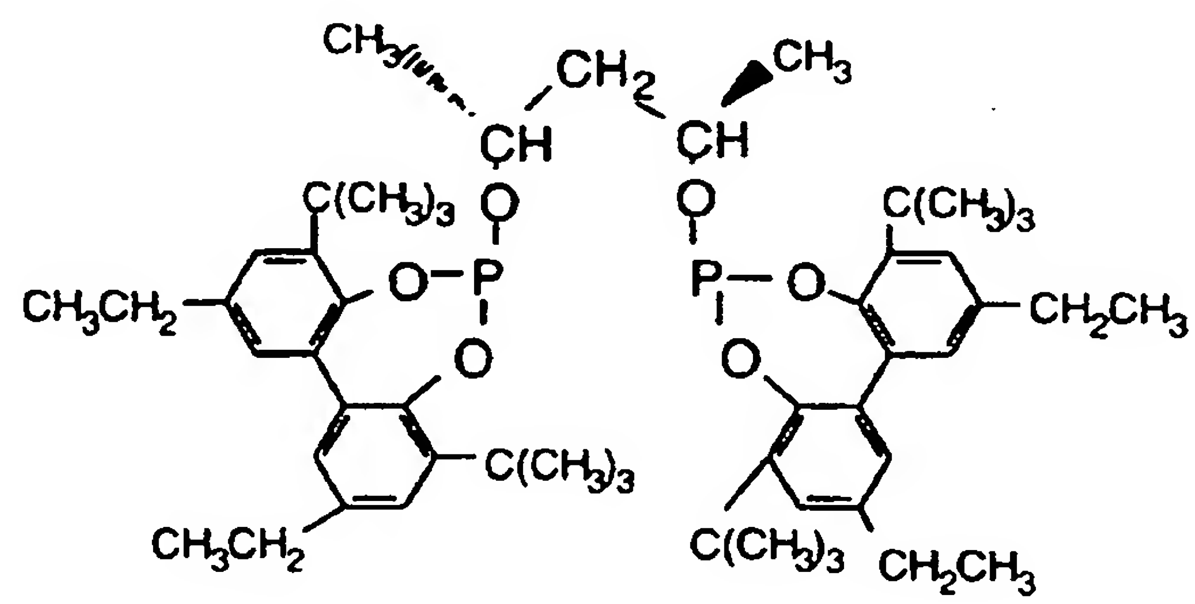
Ligand J

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethoxy-1,1'-biphenyl)]- 2,4-pentyldiphosphite having the formula:



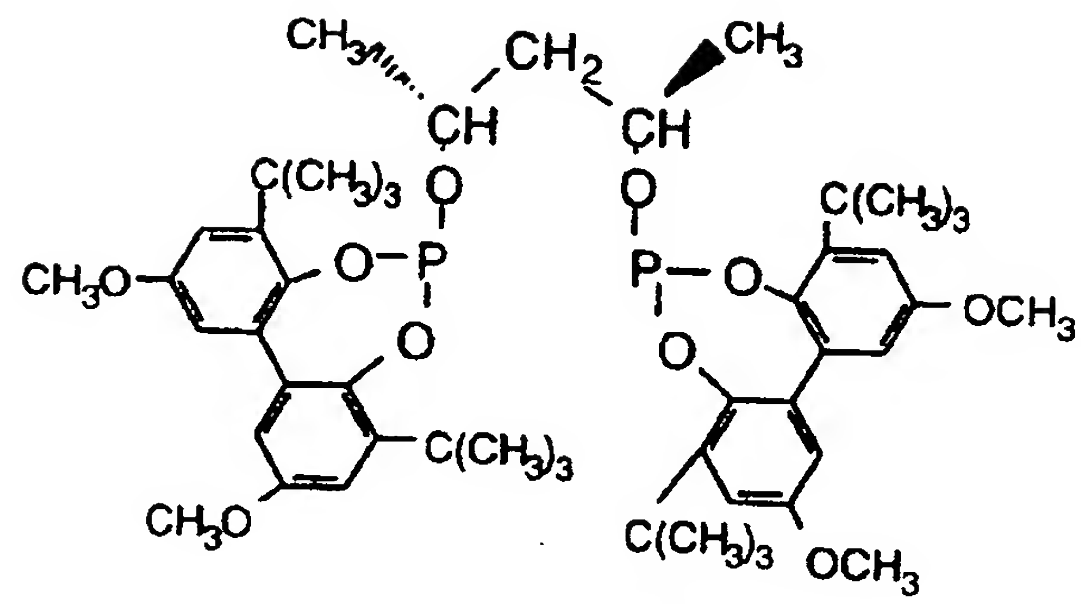
Ligand K

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-diethyl-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



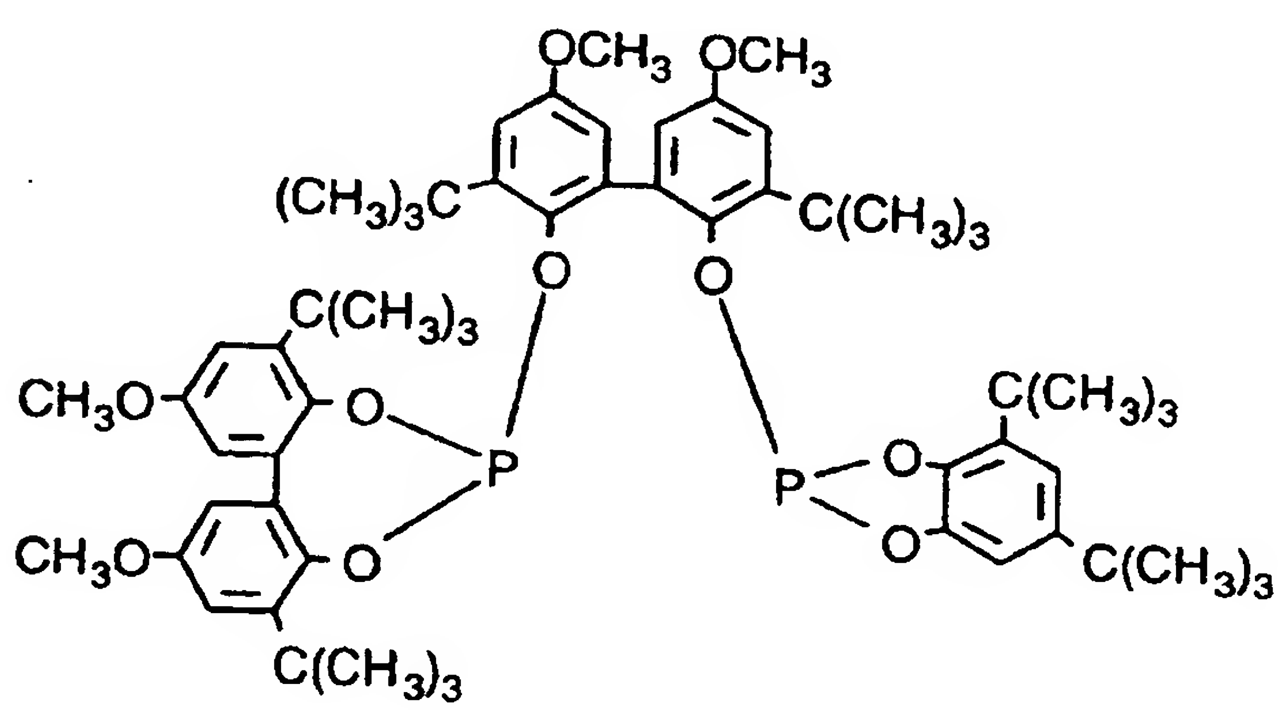
Ligand L

(2R,4R)-di[2,2'-(3,3'-di-tert-butyl-5,5'-dimethoxy-1,1'-biphenyl)]-2,4-pentyldiphosphite having the formula:



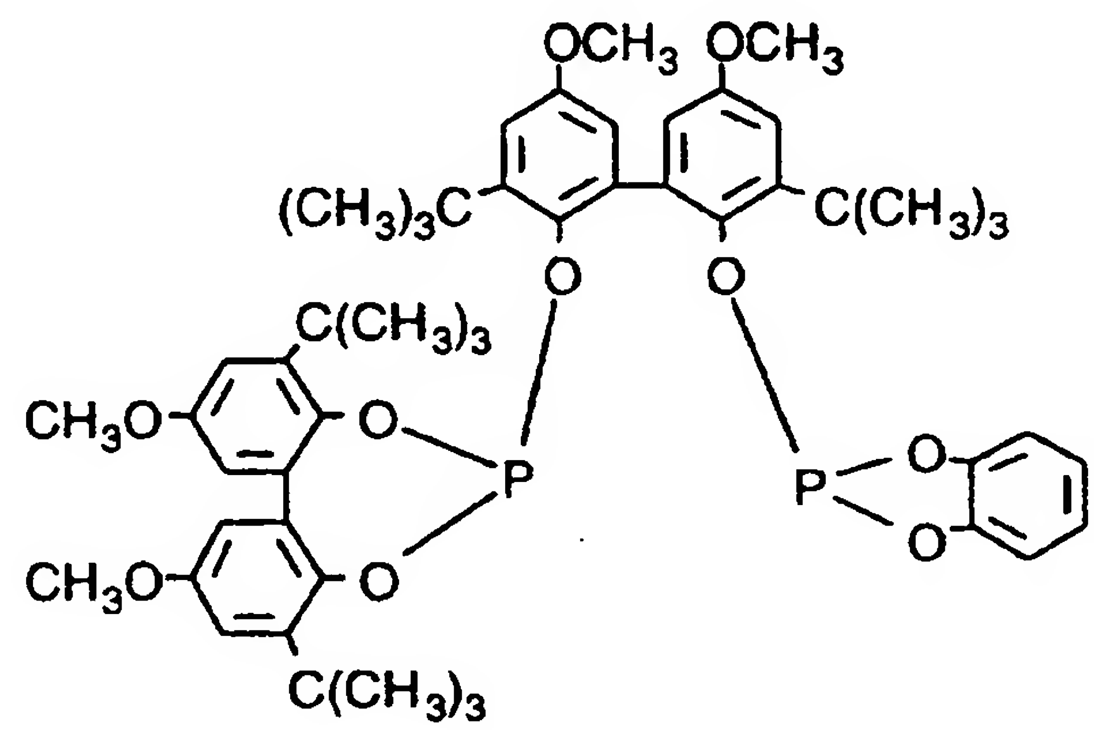

Ligand M

6-[[2'-[(4,6-bis(1,1-dimethylethyl)-1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



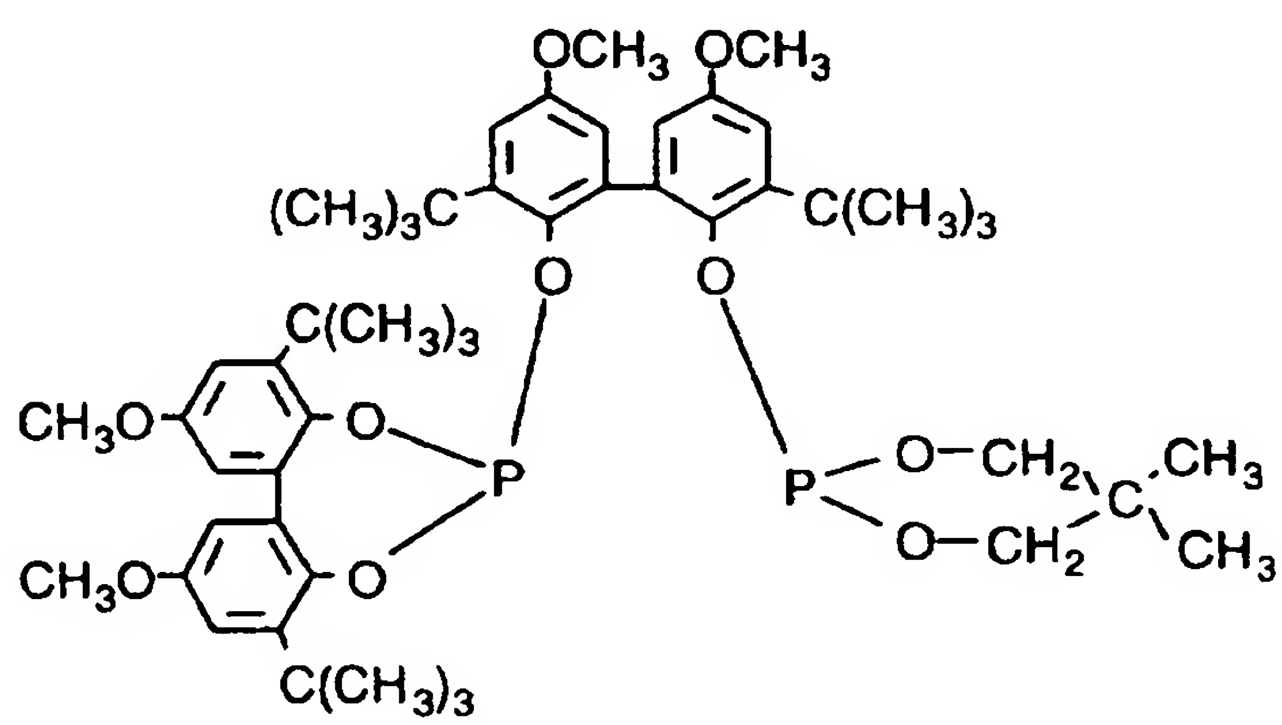

Ligand N

6-[[2'-[1,3,2-benzodioxaphosphol-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



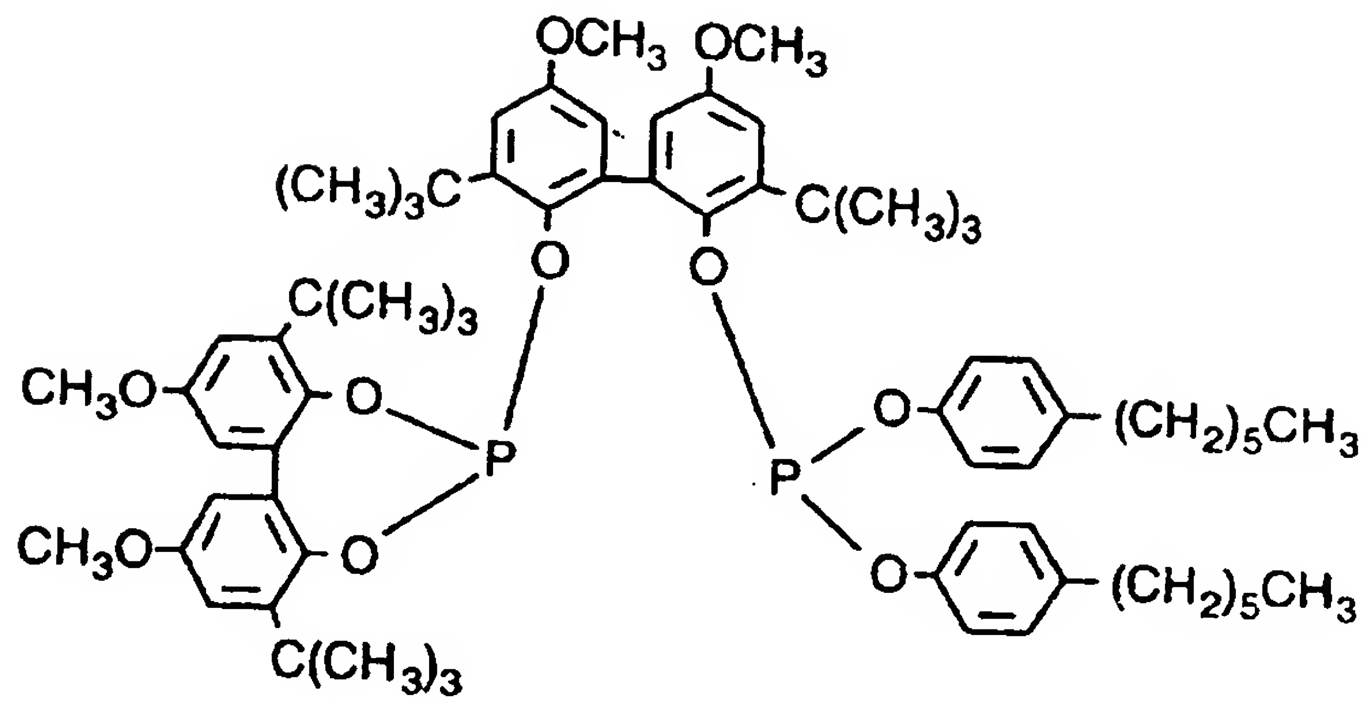
Ligand O

6-[[2'-[(5,5-dimethyl-1,3,2-dioxaphosphorinan-2-yl)oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'-biphenyl]-2-yl]oxy]-4,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]dioxaphosphepin having the formula:



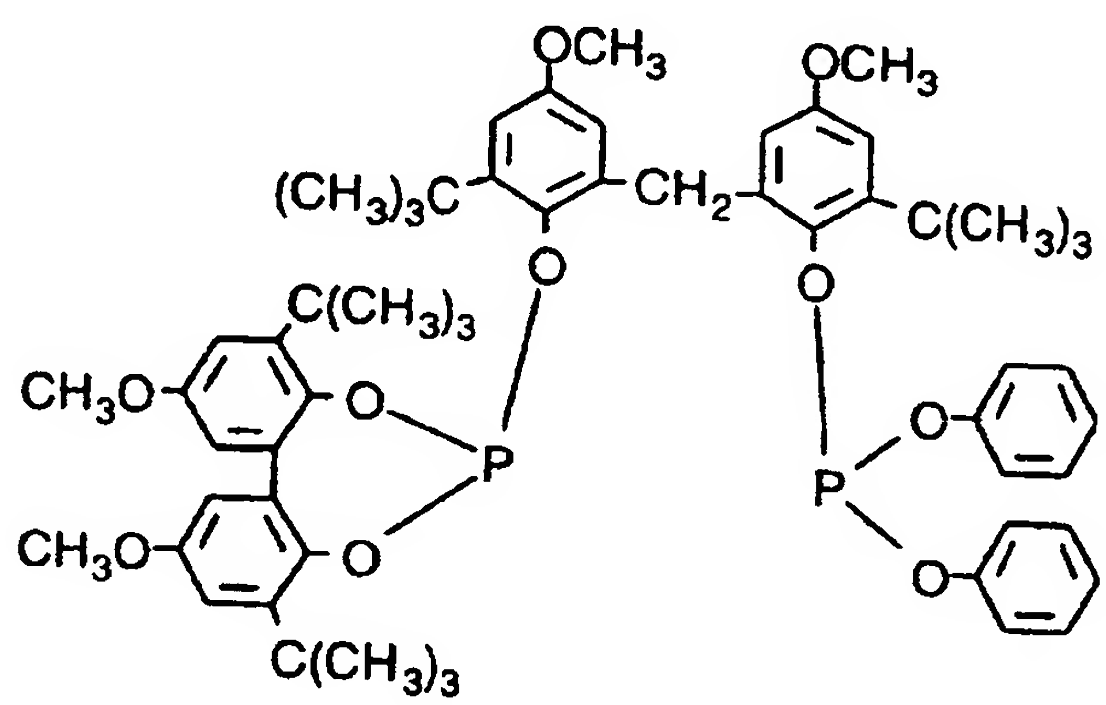
Ligand P

2'-[[4 ,8-bis(1,1-dimethylethyl)-2,10-dimethoxydibenzo[d,f][1,3,2]-dioxaphosphepin-6-yl]oxy]-3,3'-bis(1,1-dimethylethyl)-5,5'-dimethoxy[1,1'- biphenyl]-2-yl bis(4-hexylphenyl)ester of phosphorous acid having the formula:



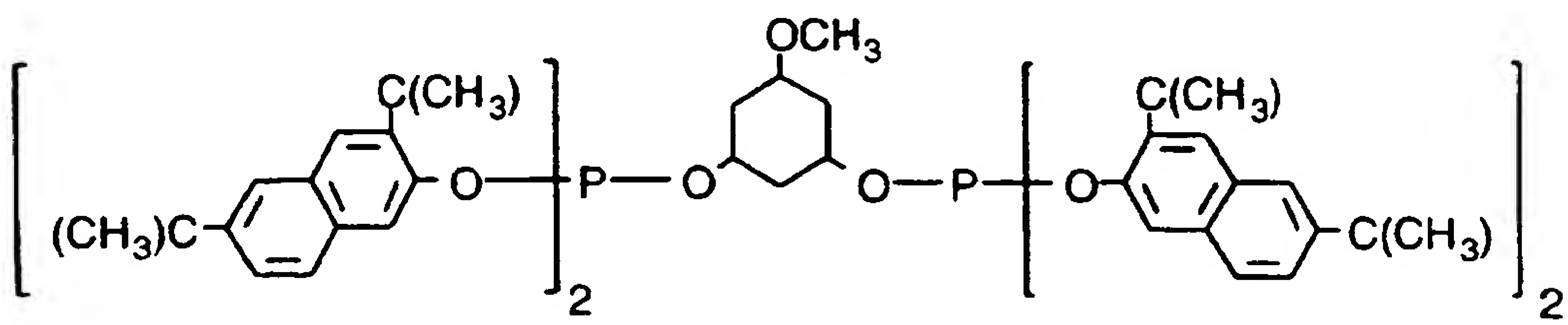
Ligand Q

2-[[2-[[4,8,-bis(1,1-dimethylethyl), 2,10-dimethoxydibenzo-[d,f][1,3,2]dioxophosphepin-6-yl]oxy]-3-(1,1-dimethylethyl)-5-methoxyphenyl]methyl]-4-methoxy, 6-(1,1-dimethylethyl)phenyl diphenyl ester of phosphorous acid having the formula:



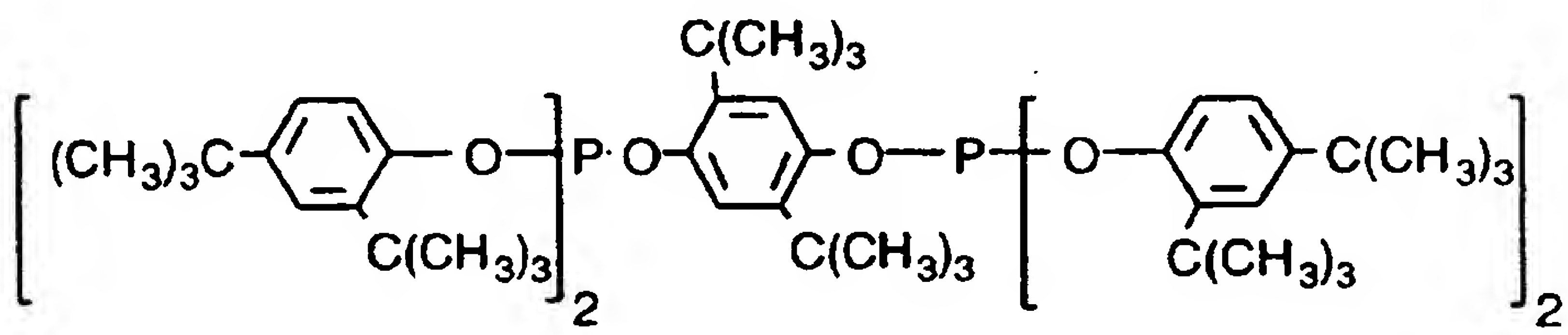
Ligand R

3-methoxy-1,3-cyclohexamethylene tetrakis[3,6-bis(1,1-dimethylethyl)-2-naphthalenyl]ester of phosphorous acid having the formula:



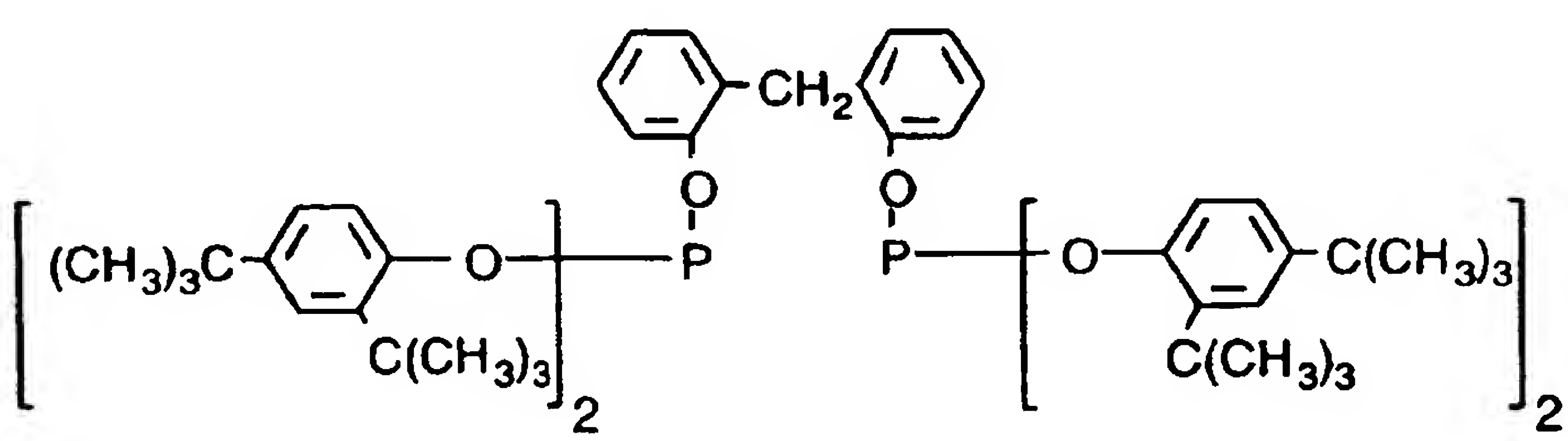
Ligand S

2,5-bis(1,1-dimethylethyl)-1,4-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



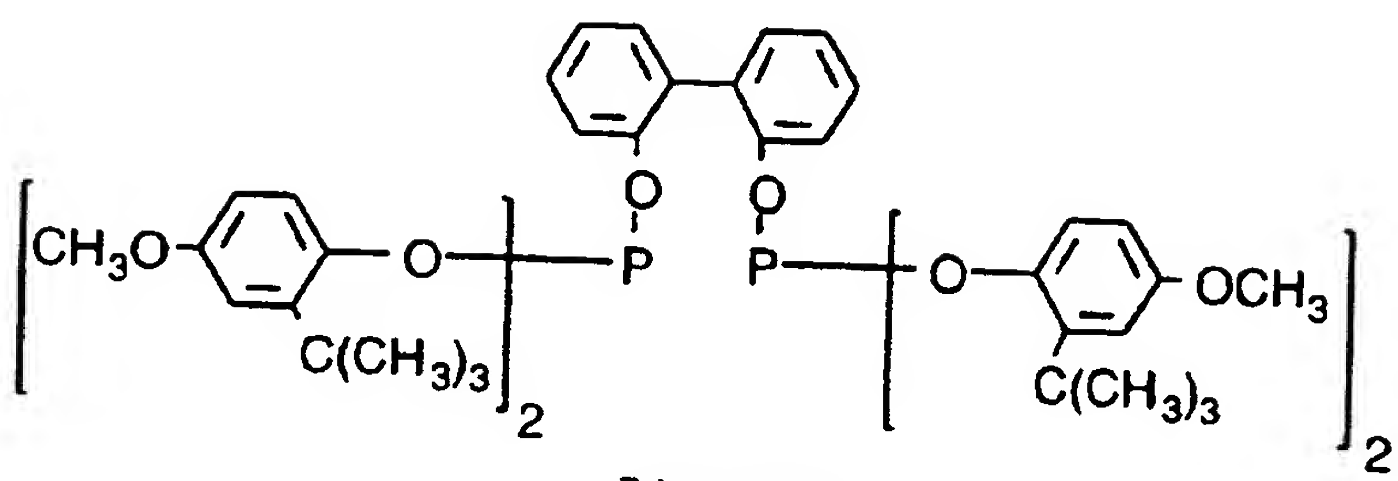
Ligand T

methylenedi-2,1-phenylene tetrakis[2,4-bis(1,1-dimethylethyl)phenyl]ester of phosphorous acid having the formula:



Ligand U

[1,1'-biphenyl]-2,2'-diyl tetrakis[2-(1,1-dimethylethyl)-4-methoxyphenyl]ester of phosphorous acid having the formula:



Ligand V

The metal-organophosphorus ligand complex catalysts employable in this invention may be formed by methods known in the art. The metal-organophosphorus ligand complex catalysts may be in homogeneous or heterogeneous form. For instance, preformed metal hydrido-carbonyl- organophosphorus ligand catalysts may be prepared and introduced into the reaction mixture of a hydroformylation process. More preferably, the metal-organophosphorus ligand complex catalysts can be derived from a metal catalyst precursor which may be introduced into the reaction medium for in situ formation of the active catalyst. For example, rhodium catalyst precursors such as rhodium dicarbonyl acetylacetonate, $Rh_2O_3$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$ and the like may be introduced into the reaction mixture along with the organophosphorus ligand for the in situ formation of the active catalyst. In a preferred embodiment of this invention, rhodium dicarbonyl acetylacetonate is employed as a rhodium precursor and reacted in the presence of a solvent with the organophosphorus ligand to form a catalytic rhodium-organophosphorus ligand complex precursor which is introduced into the reactor along with excess free organophosphorus ligand for the in situ formation of the active catalyst. In any event, it is sufficient for the purpose of this invention that carbon monoxide, hydrogen and organophosphorus compound are all ligands that are capable of being complexed with the metal and that an active metal-organophosphorus ligand catalyst is present in

the reaction mixture under the conditions used in the hydroformylation reaction.

More particularly, a catalyst precursor composition can be formed consisting essentially of a solubilized metal-organophosphorus ligand complex precursor catalyst, an organic solvent and free organophosphorus ligand. Such precursor compositions may be prepared by forming a solution of a metal starting material, such as a metal oxide, hydride, carbonyl or salt, e.g. a nitrate, which may or may not be in complex combination with a organophosphorus ligand as defined herein. Any suitable metal starting material may be employed, e.g. rhodium dicarbonyl acetylacetonate, $Rh_2O_3$, $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Rh(NO_3)_3$, and organophosphorus ligand rhodium carbonyl hydrides. Carbonyl and organophosphorus ligands, if not already complexed with the initial metal, may be complexed to the metal either prior to or in situ during the carbonylation process.

By way of illustration, the preferred catalyst precursor composition of this invention consists essentially of a solubilized rhodium carbonyl organophosphorus ligand complex precursor catalyst, an organic solvent and free organophosphorus ligand prepared by forming a solution of rhodium dicarbonyl acetylacetonate, an organic solvent and a organophosphorus ligand as defined herein. The organophosphorus ligand readily replaces one of the dicarbonyl ligands of the rhodium acetylacetonate complex precursor at room temperature as witnessed by the evolution of carbon monoxide gas. This substitution reaction may be facilitated by heating the solution if desired. Any suitable organic solvent in which both the rhodium dicarbonyl acetylacetonate complex precursor and rhodium organophosphorus ligand complex precursor are soluble can be employed. The amounts of rhodium complex catalyst precursor, organic solvent and organophosphorus ligand, as well as their preferred embodiments present in such catalyst precursor compositions may obviously correspond to those amounts employable in the

hydroformylation process of this invention. Experience has shown that the acetylacetonate ligand of the precursor catalyst is replaced after the hydroformylation process has begun with a different ligand, e.g., hydrogen, carbon monoxide or organophosphorus ligand, to form the active complex catalyst as explained above. The acetylacetone which is freed from the precursor catalyst under hydroformylation conditions is removed from the reaction medium with the product aldehyde and thus is in no way detrimental to the hydroformylation process. The use of such preferred rhodium complex catalytic precursor compositions provides a simple economical and efficient method for handling the rhodium precursor metal and hydroformylation start-up.

Accordingly, the metal-organophosphorus ligand complex catalysts used in the process of this invention consists essentially of the metal complexed with carbon monoxide and a organophosphorus ligand, said ligand being bonded (complexed) to the metal in a chelated and/or non-chelated fashion. Moreover, the terminology "consists essentially of", as used herein, does not exclude, but rather includes, hydrogen complexed with the metal, in addition to carbon monoxide and the organophosphorus ligand. Further, such terminology does not exclude the possibility of other organic ligands and/or anions that might also be complexed with the metal. Materials in amounts which unduly adversely poison or unduly deactivate the catalyst are not desirable and so the catalyst most desirably is free of contaminants such as metal-bound halogen (e.g., chlorine, and the like) although such may not be absolutely necessary. The hydrogen and/or carbonyl ligands of an active metal-organophosphorus ligand complex catalyst may be present as a result of being ligands bound to a precursor catalyst and/or as a result of in situ formation, e.g., due to the hydrogen and carbon monoxide gases employed in hydroformylation process of this invention.

As noted the hydroformylation reactions involve the use of a metal-organophosphorus ligand complex catalyst as described herein.

Of course mixtures of such catalysts can also be employed if desired. The amount of metal-organophosphorus ligand complex catalyst present in the reaction medium of a given hydroformylation reaction need only be that minimum amount necessary to provide the given metal concentration desired to be employed and which will furnish the basis for at least the catalytic amount of metal necessary to catalyze the particular hydroformylation reaction involved such as disclosed, for example, in the above-mentioned patents. In general, metal, e.g., rhodium, concentrations in the range of from about 10 ppm to about 1000 ppm, calculated as free rhodium, in the hydroformylation reaction medium should be sufficient for most processes, while it is generally preferred to employ from about 10 to 500 ppm of metal, e.g., rhodium, and more preferably from 25 to 350 ppm to metal, e.g., rhodium.

In addition to the metal-organophosphorus ligand complex catalyst, free organophosphorus ligand (i.e., ligand that is not complexed with the metal) may also be present in the hydroformylation reaction medium. The free organophosphorus ligand may correspond to any of the above-defined organophosphorus ligands discussed above as employable herein. It is preferred that the free organophosphorus ligand be the same as the organophosphorus ligand of the metal-organophosphorus ligand complex catalyst employed. However, such ligands need not be the same in any given process. The hydroformylation process of this invention may involve from about 0.1 moles or less to about 100 moles or higher, of free organophosphorus ligand per mole of metal in the hydroformylation reaction medium. Preferably the hydroformylation process of this invention is carried out in the presence of from about 1 to about 50 moles of organophosphorus ligand, and more preferably from about 1 to about 4 moles of organophosphorus ligand, per mole of metal present in the reaction medium; said amounts of organophosphorus ligand being the sum of both the amount of organophosphorus ligand that is bound (complexed)

to the metal present and the amount of free (non-complexed) organophosphorus ligand present. Since it is more preferred to produce non-optically active aldehydes by hydroformylating achiral olefins, the more preferred organophosphorus ligands are achiral type organophosphite ligands, especially those encompassed by Formula (VIII) above, and more preferably those of Formulas (IX) and (XII) above. Of course, if desired, make-up or additional organophosphorus ligand can be supplied to the reaction medium of the hydroformylation process at any time and in any suitable manner, e.g. to maintain a predetermined level of free ligand in the reaction medium.

As indicated above, the hydroformylation catalyst may be in heterogeneous form during the reaction and/or during the product separation. Such catalysts are particularly advantageous in the hydroformylation of olefins to produce high boiling or thermally sensitive aldehydes, so that the catalyst may be separated from the products by filtration or decantation at low temperatures. For example, the rhodium catalyst may be attached to a support so that the catalyst retains its solid form during both the hydroformylation and separation stages, or is soluble in a liquid reaction medium at high temperatures and then is precipitated on cooling.

As an illustration, the rhodium catalyst may be impregnated onto any solid support, such as inorganic oxides, (i.e. alumina, silica, titania, or zirconia) carbon, or ion exchange resins. The catalyst may be supported on, or intercalated inside the pores of, a zeolite or glass; the catalyst may also be dissolved in a liquid film coating the pores of said zeolite or glass. Such zeolite-supported catalysts are particularly advantageous for producing one or more regioisomeric aldehydes in high selectivity, as determined by the pore size of the zeolite. The techniques for supporting catalysts on solids, such as incipient wetness, which will be known to those skilled in the art. The solid catalyst thus formed may still be complexed with one or more of the ligands defined above. Descriptions of such solid catalysts

may be found in for example: J. Mol. Cat. 1991, 70, 363-368; Catal. Lett. 1991, 8, 209-214; J. Organomet. Chem, 1991, 403, 221-227; Nature, 1989, 339, 454-455; J. Catal. 1985, 96, 563-573; J. Mol. Cat. 1987, 39, 243-259.

The metal, e.g., rhodium, catalyst may be attached to a thin film or membrane support, such as cellulose acetate or polyphenylenesulfone, as described in for example J. Mol. Cat. 1990, 63, 213-221.

The metal, e.g., rhodium, catalyst may be attached to an insoluble polymeric support through an organophosphorus-containing ligand, such as a phosphine or phosphite, incorporated into the polymer. Such polymer-supported ligands are well known, and include such commercially available species as the divinylbenzene/polystyrene-supported triphenylphosphine. The supported ligand is not limited by the choice of polymer or phosphorus-containing species incorporated into it. Descriptions of polymer-supported catalysts may be found in for example: J. Mol. Cat. 1993, 83, 17-35; Chemtech 1983, 46; J. Am. Chem. Soc. 1987, 109, 7122-7127.

In the heterogeneous catalysts described above, the catalyst may remain in its heterogeneous form during the entire hydroformylation and catalyst separation process. In another embodiment of the invention, the catalyst may be supported on a polymer which, by the nature of its molecular weight, is soluble in the reaction medium at elevated temperatures, but precipitates upon cooling, thus facilitating catalyst separation from the reaction mixture. Such "soluble" polymer-supported catalysts are described in for example: Polymer, 1992, 33, 161; J. Org. Chem. 1989, 54, 2726-2730.

When the metal catalyst is in a heterogeneous or supported form, the reaction may be carried out in the gas phase. More preferably, the reaction is carried out in the slurry phase due to the high boiling points of the products, and to avoid decomposition of the product aldehydes. The catalyst may then be separated from the

product mixture, for example, by filtration or decantation. The reaction product fluid may contain a heterogeneous metal-organophosphorus ligand complex catalyst, e.g., slurry, or at least a portion of the reaction product fluid may contact a fixed heterogeneous metal-organophosphorus ligand complex catalyst during the hydroformylation process. In an embodiment of this invention, the metal-organophosphorus ligand complex catalyst may be slurried in the reaction product fluid.

The substituted or unsubstituted olefinic unsaturated starting material reactants that may be employed in the hydroformylation processes of this invention include both optically active (prochiral and chiral) and non-optically active (achiral) olefinic unsaturated compounds containing from 2 to 30, preferably 4 to 20, carbon atoms. Such olefinic unsaturated compounds can be terminally or internally unsaturated and be of straight-chain, branched chain or cyclic structures, as well as olefin mixtures, such as obtained from the oligomerization of propene, butene, isobutene, etc. (such as so called dimeric, trimeric or tetrameric propylene and the like, as disclosed, for example, in U. S. Patent Nos. 4,518,809 and 4,528,403). Moreover, such olefin compounds may further contain one or more ethylenic unsaturated groups, and of course, mixtures of two or more different olefinic unsaturated compounds may be employed as the starting hydroformylation material if desired. For example, commercial alpha olefins containing four or more carbon atoms may contain minor amounts of corresponding internal olefins and/or their corresponding saturated hydrocarbon and that such commercial olefins need not necessarily be purified from same prior to being hydroformylated. Further such olefinic unsaturated compounds and the corresponding aldehyde products derived therefrom may also contain one or more groups or substituents which do not unduly adversely affect the hydroformylation process or the process of this invention such as

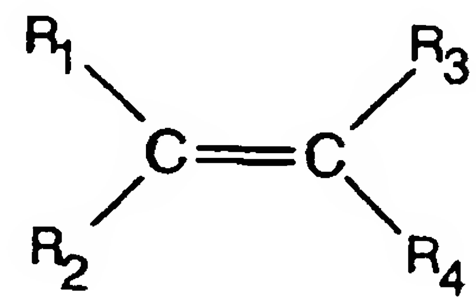
described, for example, in U. S. Patent Nos. 3,527,809, 4,769,498 and the like.

Most preferably the subject invention is especially useful for the production of non-optically active aldehydes, by hydroformylating achiral alpha-olefins containing from 2 to 30, preferably 4 to 20, carbon atoms, (including isobutylene), and achiral internal olefins containing from 4 to 20 carbon atoms as well as starting material mixtures of such alpha olefins and internal olefins.

Illustrative achiral alpha and internal olefins include, for example, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 2-butene, 2-methyl propene (isobutylene), 2-methylbutene, 2-pentene, 2-hexene, 3-hexane, 2-heptene, 2-octene, cyclohexene, propylene dimers, propylene trimers, propylene tetramers, butadiene, piperylene, isoprene, 2-ethyl-1-hexene, styrene, 4-methyl styrene, 4-isopropyl styrene, 4-tert-butyl styrene, alpha-methyl styrene, 4-tert-butyl-alpha-methyl styrene, 1,3-diisopropenylbenzene, 3-phenyl-1-propene, 1,4-hexadiene, 1,7-octadiene, 3-cyclohexyl-1-butene, and the like, as well as, 1,3-dienes, butadiene, alkyl alkenoates, e.g., methyl pentenoate, alkenyl alkanoates, alkenyl alkyl ethers, alkenols, e.g., pentenols, alkenals, e.g., pentenals, and the like, such as allyl alcohol, allyl butyrate, hex-1-en-4-ol, oct-1-en-4-ol, vinyl acetate, allyl acetate, 3-butenyl acetate, vinyl propionate, allyl propionate, methyl methacrylate, vinyl ethyl ether, vinyl methyl ether, allyl ethyl ether, n-propyl-7-octenoate, 3-butenenitrile, 5-hexenamide, eugenol, iso-eugenol, safrole, iso-safrole, anethol, 4-allylanisole, indene, limonene, beta-pinene, dicyclopentadiene, cyclooctadiene, camphene, linalool, and the like.

Prochiral and chiral olefins useful in the asymmetric hydroformylation that can be employed to produce enantiomeric

aldehyde mixtures that may be encompassed by in this invention include those represented by the formula:



(XV)

wherein $R_1$, $R_2$, $R_3$ and $R_4$ are the same or different (provided $R_1$ is different from $R_2$ or $R_3$ is different from $R_4$) and are selected from hydrogen; alkyl; substituted alkyl, said substitution being selected from dialkylamino such as benzylamino and dibenzylamino, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitro, nitrile, thio, carbonyl, carboxamide, carboxaldehyde, carboxyl, carboxylic ester; aryl including phenyl; substituted aryl including phenyl, said substitution being selected from alkyl, amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino, hydroxy, alkoxy such as methoxy and ethoxy, acyloxy such as acetoxy, halo, nitrile, nitro, carboxyl, carboxaldehyde, carboxylic ester, carbonyl, and thio; acyloxy such as acetoxy; alkoxy such as methoxy and ethoxy; amino including alkylamino and dialkylamino such as benzylamino and dibenzylamino; acylamino and diacylamino such as acetylbenzylamino and diacetylamino; nitro; carbonyl; nitrile; carboxyl; carboxamide; carboxaldehyde; carboxylic ester; and alkylmercapto such as methylmercapto. It is understood that the prochiral and chiral olefins of this definition also include molecules of the above general formula where the R groups are connected to form ring compounds, e.g., 3-methyl-1-cyclohexene, and the like.

Illustrative optically active or prochiral olefinic compounds useful in asymmetric hydroformylation include, for example, p-isobutylstyrene, 2-vinyl-6-methoxy-2-naphthylene, 3-

ethenylphenyl phenyl ketone, 4-ethenylphenyl-2-thienylketone, 4-ethenyl-2-fluorobiphenyl, 4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)styrene, 2-ethenyl-5-benzoylthiophene, 3-ethenylphenyl phenyl ether, propenylbenzene, isobutyl-4-propenylbenzene, phenyl vinyl ether and the like. Other olefinic compounds include substituted aryl ethylenes as described, for example, in U.S. Patent Nos. 4,329,507, 5,360,938 and 5,491,266, the disclosures of which are incorporated herein by reference.

Mixtures of different olefinic starting materials can be employed, if desired, in the hydroformylation reactions. More preferably the hydroformylation reactions are especially useful for the production of aldehydes, by hydroformylating alpha olefins containing from 2 to 30, preferably 4 to 20, carbon atoms, including isobutylene, and internal olefins containing from 4 to 20 carbon atoms as well as starting material mixtures of such alpha olefins and internal olefins. Commercial alpha olefins containing four or more carbon atoms may contain minor amounts of corresponding internal olefins and/or their corresponding saturated hydrocarbon and that such commercial olefins need not necessarily be purified from same prior to being hydroformylated. Illustrative mixtures of olefinic starting materials that can be employed in the hydroformylation reactions include, for example, mixed butenes, e.g., Raffinate I and II. Illustrative of suitable substituted and unsubstituted olefinic starting materials include those permissible substituted and unsubstituted olefinic compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, 1984, the pertinent portions of which are incorporated herein by reference.

The reaction conditions of the hydroformylation processes encompassed by this invention may include any suitable type hydroformylation conditions heretofore employed for producing optically active and/or non-optically active aldehydes. For instance, the total gas pressure of hydrogen, carbon monoxide and olefin starting

compound of the hydroformylation process may range from about 1 to about 10,000 psia. In general, however, it is preferred that the process be operated at a total gas pressure of hydrogen, carbon monoxide and olefin starting compound of less than about 1500 psia and more preferably less than about 500 psia. The minimum total pressure being limited predominately by the amount of reactants necessary to obtain a desired rate of reaction. More specifically the carbon monoxide partial pressure of the hydroformylation process of this invention is preferable from about 1 to about 360 psia, and more preferably from about 3 to about 270 psia, while the hydrogen partial pressure is preferably about 15 to about 480 psia and more preferably from about 30 to about 300 psia. In general $H_2$:CO molar ratio of gaseous hydrogen to carbon monoxide may range from about 1:10 to 100:1 or higher, the more preferred hydrogen to carbon monoxide molar ratio being from about 1:1 to about 10:1. Further, the hydroformylation process may be conducted at a reaction temperature from about −25°C to about 200°C. In general hydroformylation reaction temperature of about 50°C to about 120°C are preferred for all types of olefinic starting materials. Of course it is to be understood that when non-optically active aldehyde products are desired, achiral type olefin starting materials and organophosphorus ligands are employed and when optically active aldehyde products are desired prochiral or chiral type olefin starting materials and organophosphorus ligands are employed. Of course, it is to be also understood that the hydroformylation reaction conditions employed will be governed by the type of aldehyde product desired.

The hydroformylation processes encompassed by this invention are also conducted in the presence of water or an organic solvent for the metal-organophosphorus ligand complex catalyst and free organophosphorus ligand. Depending on the particular catalyst and reactants employed, suitable organic solvents include, for example, alcohols, alkanes, alkenes, alkynes, ethers, aldehydes, higher boiling

aldehyde condensation byproducts, ketones, esters, amides, tertiary amines, aromatics and the like. Any suitable solvent which does not unduly adversely interfere with the intended hydroformylation reaction can be employed and such solvents may include those disclosed heretofore commonly employed in known metal catalyzed hydroformylation reactions. Mixtures of one or more different solvents may be employed if desired. In general, with regard to the production of achiral (non-optically active) aldehydes, it is preferred to employ aldehyde compounds corresponding to the aldehyde products desired to be produced and/or higher boiling aldehyde liquid condensation byproducts as the main organic solvents as is common in the art. Such aldehyde condensation byproducts can also be preformed if desired and used accordingly. Illustrative preferred solvents employable in the production of aldehydes include ketones (e.g. acetone and methylethyl ketone), esters (e.g. ethyl acetate), hydrocarbons (e.g. toluene), nitrohydrocarbons (e.g. nitrobenzene), ethers (e.g. tetrahydrofuran (THF) and glyme), 1,4-butanediols and sulfolane. Suitable solvents are disclosed in U.S. Patent No. 5,312,996. The amount of solvent employed is not critical to the subject invention and need only be that amount sufficient to solubilize the catalyst and free ligand of the hydroformylation reaction mixture to be treated. In general, the amount of solvent may range from about 5 percent by weight up to about 99 percent by weight or more based on the total weight of the hydroformylation reaction mixture starting material.

Accordingly illustrative non-optically active aldehyde products include e.g., propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, 2-methylbutyraldehyde, hexanal, hydroxyhexanal, 2-methylvaleraldehyde, heptanal, 2-methyl 1-hexanal, octanal, 2-methyl 1-heptanal, nonanal, 2-methyl-1-octanal, 2-ethyl 1-heptanal, 3-propyl 1-hexanal, decanal, adipaldehyde, 2-methylglutaraldehyde, 2-methyladipaldehyde, 3-methyladipaldehyde, 3-hydroxypropionaldehyde, 3-pentenal, alkyl 5-formylvalerate, 2-

methyl-1-nonanal, undecanal, 2-methyl 1-decanal, dodecanal, 2-methyl 1-undecanal, tridecanal, 2-methyl 1-tridecanal, 2-ethyl, 1-dodecanal, 3-propyl-1-undecanal, pentadecanal, 2-methyl-1-tetradecanal, hexadecanal, 2-methyl-1-pentadecanal, heptadecanal, 2-methyl-1-hexadecanal, octadecanal, 2-methyl-1-heptadecanal, nonadecanal, 2-methyl-1-octadecanal, 2-ethyl 1-heptadecanal, 3-propyl-1-hexadecanal, eicosanal, 2-methyl-1-nonadecanal, heneicosanal, 2-methyl-1-eicosanal, tricosanal, 2-methyl-1-docosanal, tetracosanal, 2-methyl-1-tricosanal, pentacosanal, 2-methyl-1-tetracosanal, 2-ethyl 1-tricosanal, 3-propyl-1-docosanal, heptacosanal, 2-methyl-1-octacosanal, nonacosanal, 2-methyl-1-octacosanal, hentriacontanal, 2-methyl-1-triacontanal, and the like.

Illustrative optically active aldehyde products include (enantiomeric) aldehyde compounds prepared by the asymmetric hydroformylation process of this invention such as, e.g. S-2-(p-isobutylphenyl)-propionaldehyde, S-2-(6-methoxy-2-naphthyl)propionaldehyde, S-2-(3-benzoylphenyl)-propionaldehyde, S-2-(p-thienoylphenyl)propionaldehyde, S-2-(3-fluoro-4-phenyl)phenylpropionaldehyde, S-2-[4-(1,3-dihydro-1-oxo-2H-isoindol-2-yl)phenyl]propionaldehyde, S-2-(2-methylacetaldehyde)-5-benzoylthiophene and the like.

Illustrative of suitable substituted and unsubstituted aldehyde products include those permissible substituted and unsubstituted aldehyde compounds described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, 1984, the pertinent portions of which are incorporated herein by reference.

As indicated above, it is generally preferred to carry out the hydroformylation processes of this invention in a continuous manner. In general, continuous hydroformylation processes are well known in the art and may involve: (a) hydroformylating the olefinic starting material(s) with carbon monoxide and hydrogen in a liquid homogeneous reaction mixture comprising a solvent, the metal-

organophosphorus ligand complex catalyst, and free organophosphorus ligand; (b) maintaining reaction temperature and pressure conditions favorable to the hydroformylation of the olefinic starting material(s); (c) supplying make-up quantities of the olefinic starting material(s), carbon monoxide and hydrogen to the reaction medium as those reactants are used up; and (d) recovering the desired aldehyde hydroformylation product(s) in any manner desired. The continuous process can be carried out in a single pass mode, i.e., wherein a vaporous mixture comprising unreacted olefinic starting material(s) and vaporized aldehyde product is removed from the liquid reaction mixture from whence the aldehyde product is recovered and make-up olefinic starting material(s), carbon monoxide and hydrogen are supplied to the liquid reaction medium for the next single pass through without recycling the unreacted olefinic starting material(s). However, it is generally desirable to employ a continuous process that involves either a liquid and/or gas recycle procedure. Such types of recycle procedure are well known in the art and may involve the liquid recycling of the metal-organophosphorus complex catalyst fluid separated from the desired aldehyde reaction product(s), such as disclosed, for example, in U.S. Patent 4,148,830 or a gas cycle procedure such as disclosed, for example, in U.S. Patent 4,247,486, as well as a combination of both a liquid and gas recycle procedure if desired. The disclosures of said U.S. Patents 4,148,830 and 4,247,486 are incorporated herein by reference thereto. The most preferred hydroformylation process of this invention comprises a continuous liquid catalyst recycle process. Suitable liquid catalyst recycle procedures are disclosed, for example, in U. S. Patent Nos. 4,668,651; 4,774,361; 5,102,505 and 5,110,990.

In an embodiment of this invention, the aldehyde mixtures may be separated from the other components of the crude reaction mixtures in which the aldehyde mixtures are produced by any suitable method. Suitable separation methods include, for example,

solvent extraction, crystallization, distillation, vaporization, wiped film evaporation, falling film evaporation, phase separation, filtration and the like. It may be desired to remove the aldehyde products from the crude reaction mixture as they are formed through the use of trapping agents as described in published Patent Cooperation Treaty Patent Application WO 88/08835. A preferred method for separating the aldehyde mixtures from the other components of the crude reaction mixtures is by membrane separation. Such membrane separation can be achieved as set out in U.S. Patent No. 5,430,194 and copending U.S. Patent Application Serial No. 08/430,790, filed May 5, 1995, referred to above. The subsequent aldol condensation of the aldehyde mixtures may be conducted without the need to separate the aldehyde mixtures from the other components of the crude reaction mixtures.

As indicated above, at the conclusion of (or during) the process of this invention, the desired aldehydes may be recovered from the reaction mixtures used in the process of this invention. For example, the recovery techniques disclosed in U.S. Patents 4,148,830 and 4,247,486 can be used. For instance, in a continuous liquid catalyst recycle process the portion of the liquid reaction mixture (containing aldehyde product, catalyst, etc.), i.e., reaction product fluid, removed from the reaction zone can be passed to a separation zone, e.g., vaporizer/separator, wherein the desired aldehyde product can be separated via distillation, in one or more stages, under normal, reduced or elevated pressure, from the liquid reaction fluid, condensed and collected in a product receiver, and further purified if desired. The remaining non-volatilized catalyst containing liquid reaction mixture may then be recycled back to the reactor as may if desired any other volatile materials, e.g., unreacted olefin, together with any hydrogen and carbon monoxide dissolved in the liquid reaction after separation thereof from the condensed aldehyde product, e.g., by distillation in any conventional manner. It is generally desirable to employ an organophosphorus ligand whose molecular weight exceeds that of the

higher boiling aldehyde oligomer byproducts corresponding to the aldehydes being produced in the hydroformylation process. Another suitable recovery technique is solvent extraction or crystallization. In general, it is preferred to separate the desired aldehydes from the catalyst-containing reaction mixture under reduced pressure and at low temperatures so as to avoid possible degradation of the organophosphorus ligand and reaction products. When an alpha-mono-olefin reactant is also employed, the aldehyde derivative thereof can also be separated by the above methods.

More particularly, distillation and separation of the desired aldehyde product from the metal-organophosphorus complex catalyst containing reaction product fluid may take place at any suitable temperature desired. In general, it is recommended that such distillation take place at relatively low temperatures, such as below 150°C, and more preferably at a temperature in the range of from about 50°C to about 130°C. It is also generally recommended that such aldehyde distillation take place under reduced pressure, e.g., a total gas pressure that is substantially lower than the total gas pressure employed during hydroformylation when low boiling aldehydes (e.g., $C_4$ to $C_6$) are involved or under vacuum when high boiling aldehydes (e.g. $C_7$ or greater) are involved. For instance, a common practice is to subject the liquid reaction product medium removed from the hydroformylation reactor to a pressure reduction so as to volatilize a substantial portion of the unreacted gases dissolved in the liquid medium which now contains a much lower synthesis gas concentration than was present in the hydroformylation reaction medium to the distillation zone, e.g. vaporizer/separator, wherein the desired aldehyde product is distilled. In general, distillation pressures ranging from vacuum pressures on up to total gas pressure of about 50 psig should be sufficient for most purposes.

Aldol Condensation Step

The aldol condensation involves condensing a substituted first aldehyde, e.g., 2-methylbutyraldehyde, with a substituted or unsubstituted second aldehyde, e.g., formaldehyde, in the presence of an aldol condensation catalyst to produce a reaction mixture comprising a substituted hydroxyaldehyde, e.g., 2-ethyl-2-methyl-3-hydroxypropanal.

Illustrative substituted first aldehydes include, for example, those aldehydes produced by the hydroformylation step described above or those aldehydes produced by other conventional processes. Illustrative substituted or unsubstituted second aldehydes include, for example, formaldehyde, acetaldehyde and those aldehydes produced by the hydroformylation step described above or those aldehydes produced by other conventional processes. For purposes of this invention, the substituted first aldehyde and the substituted or unsubstituted second aldehyde can be the same or different. The amounts of substituted first aldehydes and substituted or unsubstituted second aldehydes employed in the aldol condensation step is not narrowly critical and can be any amounts sufficient to produce the substituted hydroxyaldehydes, preferably in high selectivities. Employing excess amounts of the substituted first aldehyde in the aldol condensation step may be desirable for improving product selectivity. The aldehydes, e.g., formaldehyde, may be employed as aqueous solutions.

The particular aldol condensation reaction conditions are not narrowly critical and can be any effective aldol condensation procedures sufficient to produce the substituted hydroxyaldehyde intermediates.

The aldol condensation reaction can be conducted at a temperature of from about 60°C to 120°C for a period of about 1 hour or less to about 4 hours or longer with the longer time being used at the lower temperature, preferably from about 80°C to about 100°C for

about 1 hour or less to about 2 hours or longer, and more preferably at about 85°C to 95°C for about 1 hour or less.

The aldol condensation reaction can be conducted over a wide range of pressures ranging from about 1 psig to about 300 psig. It is preferable to conduct the aldol condensation reaction at pressures of from about 5 psig to about 40 psig. The aldol condensation reaction is preferably effected in the liquid or vapor states or mixtures thereof.

The aldol condensation reaction can be conducted using known aldol condensation catalysts in conventional amounts. Illustrative of suitable aldol condensation catalysts include, for example, tertiary amines and the like. Tertiary amines that may be employed in the aldol condensation reaction include trialkylamines such as methyldiethylamine, ethyldimethylamine, tripropylamine, dimethyltertiary butylamine, and the like. Similarly, aromatic amines derived from aniline and its derivatives may be employed such as diarylalkylamines and dialkylarylamines, e.g., phenyldimethylamine, phenyldiethylamine, methyldiphenylamine, and the like. Heterocyclic tertiary amines wherein the nitrogen moiety is included as part of a heterocyclic ring may also be used effectively as aldol condensation catalysts. Such amines may include methylpiperidine, dimethylpiperazine, methylmorpholine, methylthiamorpholine, and the like. The preferred aldol condensation catalysts are trialkylamines, e.g., triethylamine.

The amount of aldol condensation catalyst used is dependent on the particular aldol condensation catalyst employed and can range from about 0.01 weight percent or less to about 10 weight percent or greater of the total weight of the starting materials.

Illustrative of substituted hydroxyaldehyde intermediates produced by the aldol condensation step include, for example, 2-ethyl-2-methyl-3-hydroxypropanal, 2,2-dimethyl-3-hydroxypropanal, 3-ethyl-2-methyl-3-hydroxypropanal, 2-ethyl-3-propyl-3-hydroxypropanal, 2,2-dimethyl-3-ethyl-3-hydroxypropanal, 2-

ethyl-3-methyl-3-propyl-3-hydroxypropanal, 2,2-diethyl-3-methyl-3-hydroxypropanal, 3-ethyl-2,2-dimethyl-3-hydroxypropanal, 2,2-dimethyl-3-ethyl-3-propyl-3-hydroxypropanal, 2-methyl-2-propyl-3-hydroxypropanal, 2,3-dimethyl-3-ethyl-2-propyl-3-hydroxypropanal, 2,3-dipropyl-3-ethyl-2-methyl-3-hydroxypropanal, 2-butyl-2-ethyl-3-hydroxypropanal, 2-butyl-2,3-diethyl-3-methyl-3-hydroxypropanal, 2-butyl-2,3-diethyl-3-propyl-3-hydroxypropanal, 3-butyl-2-propyl-3-hydroxypropanal and the like.

The substituted hydroxyaldehyde intermediates produced by the aldol condensation step of this invention can be separated by conventional techniques such as distillation or other suitable means. For example, a crude reaction product can be subjected to a distillation-separation at atmospheric or reduced pressure through a packed distillation column. Reactive distillation may be useful in conducting the aldol condensation reaction step. The subsequent hydrogenation of the aldol condensation reaction mixtures may be conducted without the need to separate the hydroxyaldehydes from the other components of the crude reaction mixtures.

Hydrogenation Step

The particular hydrogenation reaction conditions are not narrowly critical and can be any effective hydrogenation procedures sufficient to produce the substituted hydrocarbon diols of this invention. In a preferred embodiment, it has been found that the combination of relatively low temperatures and low hydrogen pressures as described below provide good reaction rates and high product selectivities. The hydrogenation reaction may proceed in the presence of water, e.g., less than about 40 weight percent water, without substantial degradation of the hydrogenation catalyst.

The hydrogenation reaction can be conducted at a temperature of from about 60°C to 180°C for a period of about 1 hour or less to about 12 hours or longer with the longer time being used at

the lower temperature, preferably from about 80°C to about 140°C for about 1 hour or less to about 8 hours or longer, and more preferably at about 115°C to 125°C for about 1 hour or less to about 3 hours or longer. During the hydrogenation reaction, from less than 0.01 percent by weight to about 5 percent by weight of the total weight of the starting materials, preferably from about 0.01 percent by weight to about 2 percent by weight, of a free radical inhibitor can be added to the reaction mass. Illustrative of such free radical inhibitors are 2,6-ditertiarybutyl-4-methyl phenol, hydroquinone, hydroquinone monomethyl ether, and the like. A particularly useful inhibitor is hydroquinone.

The hydrogenation reaction can be conducted over a wide range of hydrogen pressures ranging from about 50 psig to about 10000 psig, preferably from about 200 psig to about 1500 psig. It is most preferable to conduct the hydrogenation reaction at hydrogen pressures of from about 500 psig to about 1000 psig. The reaction is preferably effected in the liquid or vapor states or mixtures thereof.

In the presence of a suitable hydrogenation catalyst, e.g., a manganese oxide-promoted copper oxide/copper chromite hydrogenation catalyst, a favorable weight hourly space velocity can be practiced. Even at hydrogenation pressures as low as 500 psig, a weight hourly space velocity of 1.0 $hour^{-1}$ to 0.1 $hour^{-1}$ can be maintained. Higher hydrogenation pressures are not required to maintain these favorable space velocities and the favorable yields and process economics for the substituted hydrocarbon diols obtained therefrom.

The hydrogenation reaction can be conducted using known hydrogenation catalysts in conventional amounts. Illustrative of suitable hydrogenation catalysts include, for example, Raney-type compounds such as Raney nickel and modified Raney nickels; molybdenum-promoted nickel, chromium-promoted nickel, cobalt-promoted nickel; platinum; palladium; iron; cobalt molybdate on

alumina; copper chromite; barium promoted copper chromite; tin-copper couple; zinc-copper couple; aluminum-cobalt; aluminum-copper; and aluminum-nickel; platinum; nickel; and the like. The preferred catalysts are manganese-promoted copper-chromate heterogeneous catalysts, e.g., manganese oxide-promoted copper oxide/copper chromite catalysts. See, for example, U.S. Patent Nos. 4,855,515 and 4,393,251, the disclosures of which are incorporated herein by reference.

The amount of catalyst used in the hydrogenation reaction is dependent on the particular catalyst employed and can range from about 0.01 weight percent or less to about 10 weight percent or greater of the total weight of the starting materials.

Illustrative of substituted 1,3-propanediols prepared by the processes of this invention include, for example, 2-ethyl-2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 3-ethyl-2-methyl-1,3-propanediol, 2-ethyl-3-propyl-1,3-propanediol, 2,2-dimethyl-3-ethyl-1,3-propanediol, 2-ethyl-3-methyl-3-propyl-1,3-propanediol, 2,2-diethyl-3-methyl-1,3-propanediol, 3-ethyl-2,2-dimethyl-1,3-propanediol, 2,2-dimethyl-3-ethyl-3-propyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2,3-dimethyl-3-ethyl-2-propyl-1,3-propanediol, 2,3-dipropyl-3-ethyl-2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butyl-2,3- diethyl-3-methyl-1,3-propanediol, 2-butyl-2,3-diethyl-3-propyl-1,3-propanediol, 3-butyl-2-propyl-1,3-propanediol and the like.

The substituted hydrocarbon diols and, in particular, the substituted 1,3-propanediols preferably have (i) a non-symmetrical structure which contributes to increased flexibility while maintaining hardness, low viscosity and low crystallinity, (ii) primary hydroxyl groups which contribute to energy efficiency and low resin color, and (iii) no beta hydrogen which contributes to increased stability of ester linkage and excellent weatherability.

The substituted hydrocarbon diol products produced by the processes of this invention can be separated by conventional techniques such as distillation. For example, a crude reaction product can be subjected to a distillation-separation at atmospheric or reduced pressure through a packed distillation column. Reactive distillation may be useful in conducting certain reaction steps of this invention. Saponification (sodium hydroxide) can be used to remove ester byproducts and for recovery of catalyst.

The substituted hydrocarbon diol processes of this invention may be carried out using, for example, a fixed bed reactor, a fluid bed reactor, or a slurry reactor. The optimum size and shape of the catalysts will depend on the type of reactor used. In general, for fluid bed reactors, a small, spherical catalyst particle is preferred for easy fluidization. With fixed bed reactors, larger catalyst particles are preferred so the back pressure within the reactor is kept reasonably low.

The substituted hydrocarbon diol processes of this invention can be conducted in a batch or continuous fashion, with recycle of unconsumed starting materials if required. The reaction can be conducted in a single reaction zone or in a plurality of reaction zones, in series or in parallel or it may be conducted batchwise or continuously in an elongated tubular zone or series of such zones. The materials of construction employed should be inert to the starting materials during the reaction and the fabrication of the equipment should be able to withstand the reaction temperatures and pressures. Means to introduce and/or adjust the quantity of starting materials or ingredients introduced batchwise or continuously into the reaction zone during the course of the reaction can be conveniently utilized in the processes especially to maintain the desired molar ratio of the starting materials. The reaction steps may be effected by the incremental addition of one of the starting materials to the other. Also, the reaction steps can be combined by the joint addition of the

starting materials. When complete conversion is not desired or not obtainable, the starting materials can be separated from the product, for example by distillation, and the starting materials then recycled back into the reaction zone.

The processes are conducted for a period of time sufficient to produce the substituted hydrocarbon diol products. The exact reaction time employed is dependent, in part, upon factors such as temperature, nature and proportion of starting materials, and the like. The reaction time will normally be within the range of from about one-half to about 100 hours or more, and preferably from less than about one to about ten hours.

The process may be conducted in either glass lined, stainless steel or similar type reaction equipment. The reaction zone may be fitted with one or more internal and/or external heat exchanger(s) in order to control undue temperature fluctuations, or to prevent any possible "runaway" reaction temperatures.

The substituted hydrocarbon diols useful in this invention, including the substituted hydroxyaldehyde intermediates, can undergo further reaction(s) to afford desired derivatives thereof. Such permissible derivatization reactions can be carried out in accordance with conventional procedures known in the art. Illustrative derivatization reactions include, for example, esterification, etherification, alkoxylation, amination, alkylation, hydrogenation, dehydrogenation, reduction, acylation, condensation, carboxylation, oxidation, silylation and the like, including permissible combinations thereof. This invention is not intended to be limited in any manner by the permissible derivatization reactions or permissible derivatives of substituted hydrocarbon diols or substituted hydroxyaldehydes.

More particularly, the substituted hydrocarbon diols useful in this invention can undergo any of the known reactions of hydroxyl groups illustrative of which are reactions with acyl halides to

form esters; with ammonia, a nitrile, or hydrogen cyanide to form amines; with alkyl acid sulfates to form disulfates; with carboxylic acids and acid anhydrides to form esters and polyesters; with alkali metals to form salts; with ketenes to form esters; with acid anhydrides to form carboxylic acids; with oxygen to form aldehydes and carboxylic acids; ring-opening reactions with lactones, tetrahydrofuran, and alkylene oxides such as ethylene oxide, propylene oxide, epichlorohydrin; dehydrogenation to form aldehydes, isocyanates to form urethanes, and the like.

Illustrative derivatives based on the substituted hydrocarbon diols that are useful in preparing the polyurethanes of this invention include, for example, polyesters, silicone-containing compounds, polyols initiated with said substituted hydrocarbon diols, and the like, including mixtures thereof. This invention is not intended to be limited in any manner by the permissible derivatives of hydrocarbon diols.

The polyester derivative products useful in this invention can be prepared from certain substituted hydrocarbon diols and/or derivatives of said substituted hydrocarbon diols, polyfunctional carboxylic acids and/or acid anhydrides, and optionally other polyols.

Optionally, up to about 60 weight percent, preferably up to about 40 weight percent of other di-, tri-, tetra-, and higher-functionality polyols may be used in combination with the substituted hydrocarbon diols of formula (I) to form the polyester derivatives. Suitable polyols include, for example, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, polyoxypropylene diols and triols, neopentyl glycol, esterdiols such as 2-methyl-2-hydroxymethylbutyl 2-methyl-2-hydroxymethylbutyrate and 2-methyl-2-hydroxymethylpropyl 2-methyl-2-hydroxymethylpropionate and ethoxylated and propoxylated esterdiols, ethylene oxide/propylene oxide copolymer polyols, polyether polyols, polycarbonate polyols, poly(alkylene oxide) polyols, 1,3-propanediols other than those of

formula (II), 1,4-butanediols, poly(tetramethylene oxide) polyols, 1,5-pentanediols, 1,6-hexanediols, 2-ethyl-1,3-hexanediol, 1,7-heptanediol, and higher linear and branched hydrocarbon diols, polylactone diols and triols such as the poly-epsilon-caprolactone polyols; halogenated diols such as 3-chloro-1,2-propanediol, 2,3-dibromo-1,4-butanediol; triols and higher hydroxyl-functional polyols such as trimethylolpropane, pentaerythritol, dipentaerythritol, sorbitol, sucrose; hydroquinone and substituted hydroquinones, bisphenols such as Bisphenol A, Bisphenol C, Bisphenol F, as well as others; 1,2-cyclohexanediols, 1,3-cyclohexanediols, 1,4-cyclohexanediols, 1,4-cyclohexane dimethanol, xylenediols, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, and the like, including mixtures thereof.

Illustrative of the polyfunctional carboxylic acids that can be used to prepare the polyester derivative products useful in this invention include, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, tridecanedioic acid, maleic acid, fumaric acid, 2-methyl-cis-2-butenedioic acid, 2-methylenesuccinic acid, 1,1-cyclobutanedicarboxylic acid, norcamphoric acid, tetrahydrophthalic acid, methyl-tetrahydrophthalic acid, 1,1-cyclohexanedicarboxylic acid, hexahydrophthalic acid, 1,4-cyclohexanedicarboxylic acid, chlorendic acid, 1,4-benzenediacetic acid, phthalic acid, isophthalic acid, trimellitic acid, any other polyfunctional carboxylic acid including those having substituents thereon such as alkyl or alkoxy groups, nitro, halogen, aryl, carboxyl or any other group that will not unduly interfere with the reaction and the like as well as mixtures of such acids and mixtures of such acids with acid anhydrides.

Illustrative of the acid anhydrides that can be used to prepare the polyester derivative products useful in this invention include, for example, trimellitic anhydride, tetrahydrophthalic anhydride, phthalic anhydride, isophthalic anhydride, benzophenone

dicarboxylic acid anhydride, succinic anhydride, glutaric anhydride, napthoic anhydride, clorendic anhydride, itaconic anhydride, maleic anhydride, or any other intramolecular anhydride including those having substituents thereon such as alkyl or alkoxy groups, nitro, halogen, aryl, carboxyl or any other group that will not unduly interfere with the reaction and the like as well as mixtures of anhydrides or mixtures of anhydrides and polyfunctional carboxylic acids.

The polyester derivatives can be prepared by heating conventional amounts of the substituted hydrocarbon diols, optional polyols, polyfunctional carboxylic acids and/or acid anhydrides at an elevated temperature and removing water of condensation. The process of condensation is rate enhanced if catalysts are used. The catalysts that may be used to prepare the polyesters useful in the compositions of this invention are those known to persons skilled in the art of polyester preparation, illustrative of which are dibutyltin oxide, antimony oxide, tin oxide, titanium alkoxides, alkali metal salts or metallic salts of manganese, cadmium, magnesium, zinc, cobalt, tin, and the like.

Products containing free carboxylic acid groups can be made by conventional methods by reacting the substituted hydrocarbon diols of formula (I) with acid anhydrides in which one equivalent of acid anhydride is used for each equivalent of hydroxyl.

The product containing free carboxylic acid groups can be prepared by heating the substituted hydrocarbon diol of formula (I) and an acid anhydride at a temperature of about 60°C to about 200°C, preferably from about 80°C to about 160°C, and most preferably from about 100°C to about 140°C for a period of time ranging from about 30 minutes to about 8 hours or more, preferably from about 1 hour to about 4 hours, or until substantially all of the acid anhydride has reacted with the hydroxyl groups. Usually about 0.10 to about 1.0 equivalent of anhydride are used per equivalent of hydroxyl, preferably

about 0.25 to about 1.0 equivalent of anhydride per equivalent of hydroxyl, and most preferably from about 0.85 to about 1.0 equivalent of anhydride per equivalent of hydroxyl. If desired, the reaction may be carried out in the presence of a solvent that is inert to reaction with hydroxyl groups or anhydride groups such as benzene, toluene, methyl ethyl ketone, methyl i-butyl ketone, methyl amyl ketone, ethoxyethyl acetate, ethoxyethyl butyrate, and the like.

Illustrative of the anhydrides that can be used in preparation of the free carboxylic acid products include, for example, tetrahydrophthalic anhydride, phthalic anhydride, isophthalic anhydride, benzophenone dicarboxylic acid anhydride, succinic anhydride, glutaric anhydride, napthoic anhydride, chlorendic anhydride, maleic anhydride, itaconic anhydride, or another intramolecular anhydride including those having substituents thereon such as alkyl or alkoxy groups, nitro, halogen, aryl, carboxyl, or any other group that will not unduly interfere with the reaction, and the like as well as mixtures of anhydrides.

If desired, a catalyst may be used in preparation of the free carboxylic acid products. Illustrative of the catalysts that can be used to prepare the free carboxylic acid products of this invention are dibutyltin dioxide, antimony oxide, tin oxide, titanium alkoxides, alkali metal salts or metallic salts of manganese, cadmium, magnesium, zinc, tin, and the like.

The free carboxylic acid products, e.g., substituted 1,3-dicarboxylic acids, can be used in combination with polyols, including formula (I) substituted hydrocarbon diols, having two or more hydroxyl groups to produce polyesters that can be used in coatings, adhesives, inks, fibers, fabrics, shaped articles, and the like.

Ester products can be prepared by conventional methods by reacting formula (I) substituted hydrocarbon diols with an anhydride such as acetic anhydride which would form the dimethyl ester when one equivalent of acetic anhydride is reacted with each

equivalent of formula (I) substituted hydrocarbon diols. It is understood by those skilled in the art that less than a 1:1 equivalency of anhydride per hydroxyl group will result in a partially esterified product that will contain both ester and hydroxyl groups. Esterified and partially esterified products such as these are useful as inert solvents or intermediates for further reaction through free hydroxyl groups or through transesterification with suitable compounds including themselves.

Silicone-containing compounds can be prepared by conventional methods by either end capping, coupling, or other reaction when formula (I) substituted hydrocarbon diols or mixtures of formula (I) substituted hydrocarbon diols and optionally other polyols are reacted with silanes. It is understood by those skilled in the art that when polyfunctional compounds are combined, a variety of products, including chain extended products, can be obtained. Illustrative of the silanes include, for example, chloroalkylchloro and arylchlorosilanes, diphenylethylchlorosilane, trimethylchlorosilane, dimethyldichloromethylsilane, triphenylchlorosilane, methyldichlorsilane, dimethylethylchlorosilane, dichlorosilane; alkoxysilanes such as methoxysilane, dimethoxysilane, diethyoxysilane, triethoxysilane, dimethylmethoxychlorsilane, dimethylmethoxysilane, tris(methoxy)-3-chloropropylsilane, and the like.

The silicone-containing compounds can be used as solvents, surfactants, reactive diluents or other components, as hydraulic fluids, as intermediates for the formation of other compounds, as components in polyesters that have utility in coatings, inks, adhesives, fibers, and molded articles, as well as in other end uses.

Illustrative polyols that can be used in combination with the formula (I) substituted hydrocarbon diols to prepare derivatives thereof include, for example, diethylene glycol, 1,4-

butanediol, 1,6-hexanediol, 1,4-dihydroxyquinone, 2,2-dimethyl-1,3-propanediol, hydroxyl-terminated polyesters, ethylene oxide/propylene oxide copolymer polyols, poly(ethylene oxide) polyols, poly(propylene oxide) polyols, poly(alkylene oxide) polyols, poly(tetramethylene oxide) polyols, polyether polyols, polycarbonate polyols, polylactone polyols, and the like, including mixtures thereof.

Polylactone polyols can be prepared by conventional methods by reacting from 1 to 50 moles, preferably from 1 to 25, and most preferably from 1 to 10 moles of a lactone with one mole of one of the substituted hydrocarbon diols of this invention. Illustrative of the lactones that can be used include, for example, epsilon-caprolactone, epsilon-methyl-epsilon-caprolactone, gamma-methyl-epsilon-caprolactone, gamma-methyl-epsilon-methyl-epsilon-caprolactone, delta-valerolactone and alkyl or aryl substituted delta-valerolactones, delta-enantolactone and alkyl or aryl substituted delta-enantolactone, beta-propriolactone, and the like. The polylactone polyols are prepared by heating the lactone and substituted hydrocarbon diol at a temperature of about 140°C to about 210°C, preferably from about 150°C to about 180°C for a period of time of about 6 hours to about 36 hours, preferably from 8 hours to about 24 hours. It is preferred to use from about 10 to 5000 or more parts per million, preferably from about 20 to about 1500 parts per million, of a catalyst to promote the ring-opening polymerization. Illustrative of such catalysts are the organometallics such as stannous octanoate, dibutyltin dilaurate, zinc octanoate, and the like. Such polylactone polyols have many uses, illustrative of which are intermediates for the preparation of polyurethane elastomers and foams, aminoplast-cured coatings, radiation-cured coatings and inks, and the like. Use of the substituted hydrocarbon diols of this invention in preparation of the polyols may result in improved hydrolytic stability for materials prepared from the polylactone polyols.

In an embodiment of this invention, certain substituted hydroxyaldehyde intermediates can be isolated and used in a variety of ways including as reactive diluents for cycloaliphatic epoxide systems that are curable by either thermal means when cation-generating catalysts/initiators such as boron trifluoride, boron trifluoride etherate, triflic acid or its salts such as diethyl ammonium triflate, ammonium triflate, and the like are used, or by photochemical means when photolyzable Bronsted or Lewis acid-generating photoinitiators such as the onium salts which can be illustrated by the arylsulfonium hexafluorophosphates, the arylsulfonium hexafluoroarsenates, the arylsulfonium hexafluoroantimonates, diazonium hexafluorophosphate, iodonium hexafluorophosphate, iodonium hexafluoroantimonates, and the like are used.

The substituted hydrocarbon diols, particularly those substituted 1,3-propanediols encompassed within formulas (I) and (II), may be useful in a number of ways including imparting excellent physical characteristics, such as water resistance, chemical resistance and the like, to coatings, inks, adhesives, and sealants prepared from the polyurethanes of this invention.

The preferred isocyanate-terminated polyurethanes of this invention can be prepared by reacting a formula (II) substituted 1,3-propanediol with a polyfunctional isocyanate to form isocyanate-terminated polymers.

The amount of hydrocarbon diol and polyol to be used for preparation of the polyurethanes of this invention is not narrowly critical; however, it is preferably equal to the number of equivalents of isocyanate minus one so that an essentially isocyanate-capped polyurethane is obtained.

It is understood by those skilled in the art that higher molecular weight species can form by chain extension during the reaction in which the hydrocarbon diol is capped with the multifunctional isocyanate, and that branched structures of higher

molecular weight can be formed. A wide variety of modifying polyols can be added to the formula (II) substituted 1,3-propanediols when the polyurethanes are prepared or said polyols can be used as the one of the packages in two-package polyurethanes which contain polyurethane products as one of the packages. In a specific embodiment of this invention, monoisocyanates can be used to partially cap the hydrocarbon diols of the invention and impart special properties such as flame resistance when halogenated aryl monoisocyanates are used.

Illustrative of the polyfunctional isocyanates that can be used to prepare the polyurethanes of this invention include, for example, 2,4-toluene diisocyanate and 2,6-toluene diisocyanate as well as mixtures of 2,4- and 2,6-toluene diisocyanate; 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-dicyclohexyldiisocyanate or reduced MDI, meta- and para-tetramethyl xylene diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate, hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylenehexamethylene diisocyanate, meta- and para-phenylene diisocyanate, isophorone diisocyanate; 2,4-, 2-6- and 2,4-/2,6-bromotoluene diisocyanate, 4-bromo-meta-phenylene diisocyanate, ortho- and meta-trifluoromethylphenylisocyanate; ortho, meta-, and para-fluorophenylisocyanate; 4,6-dibromo-meta-phenylene diisocyanate; ortho-, meta-, and para-chlorophenyl isocyanate, 4,4',4"-triisocyanatotriphenylmethane, and the like, including mixtures thereof.

Other polyols can be used in combination with the particular formula (II) substituted 1,3-propanediols when the polyurethanes of this invention are prepared. The polyols contain two or more free hydroxyl groups, preferably from about two to about eight, and most preferably from two to about three free hydroxyl groups. Of particular interest are Type II or Type III polyurethanes that contain minor amounts of from about less than one percent by weight to about 45 percent by weight, preferably from about one to about 25 weight

percent, and most preferably from about one to about 15 weight percent of a tri- or higher hydroxyl functionality polyol.

Illustrative of the polyols useful for addition to the formula (II) substituted 1,3-propanediols to form the polyurethanes of this invention include, for example, ethylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 2,2,4-trimethyl-1,5-pentanediol, esterdiols such as 2-methyl-2-hydroxymethylbutyl 2-methyl-2-hydroxymethylbutyrate and 2-methyl-2-hydroxymethylpropyl 2-methyl-2-hydroxymethylpropionate and ethoxylated and propoxylated esterdiols, trimethylolpropane, ethoxylated and propoxylated trimethylolpropane, 1,4-cyclohexane dimethanol, 1,4-phenylene dimethanol; the various caprolactone polyols including di- and trifunctional caprolactone polyols such as TONE® -0200, -0210, -0230, -0240, -0260, -0301, -0305, and -0310 which are commercially available from Union Carbide Corporation; propylene glycol and poly(propylene oxide) polyols, poly(tetramethylene oxide) polyols, polyester polyols, polyether polyols, poly(alkylene oxide) polyols, polyoxyethylene polyols, polycarbonate polyols, and the like, including mixtures thereof.

Catalysts that can be used to catalyze the isocyanate/hydroxyl reaction that is involved in urethane linkage formation are known to those skilled in the art. Illustrative of such catalysts which can be used in conventional amounts include organometallics such as stannous octanoate, zinc octanoate, dibutyltin dilaurate; amines such as the alkanolamines, tetramethyldiamines; and the like.

Catalysts that can be used to promote the moisture cure of polyurethanes are known to those skilled in the art. Illustrative of such catalysts are amines, alkanol amines, and organometallics such as methyl diethanolamine, cobalt naphthenate, lead naphthenate, dibutyltin dilaurate, and the like.

Blocked compounds that can be used to promote curing of polyurethanes include Schiff bases as described by G. Schleier and F. Gerold in Proceedings of Polyurethanes World Congress 1987 held in Aachen, Germany on 09/29-02/87, pages 323-327, phenol-blocked isocyanates including phenol derivatives of the isocyanate-terminated compounds, blocked amines, and the like. When such blocked compounds are employed, it is necessary to heat the coating system to a temperature such that unblocking will occur which can be from about 100°C to about 200°C. If only blocked isocyanates are involved, it is necessary to cool the deblocked systems to room temperature and allow moisture to cause curing. If polyols are added or if blocked amines are employed, curing will take place in the absence of moisture at the elevated temperature.

When two-package polyurethanes are made from the isocyanate-terminated compounds of this invention, the optional modifying polyols can also be used individually or in admixture as one of the two-packages.

Illustrative polyurethanes and coatings prepared therefrom are described in European Patent Application No. 0542220, published May 19, 1993, in which the hydrocarbon diols useful in this invention can be substituted for the hydrocarbon diols described in European Patent Application No. 0542220, the disclosure of which is incorporated herein by reference.

Thermoplastic polyurethanes that can be used for molding shaped articles, elastomers, fibers, or in solution form as coatings can be prepared from diisocyanate terminated compounds of this invention. If desired, small amounts of trifunctional or higher functionality isocyanates and/or polyols can be used to alter toughness and other properties. The amount of these higher functionality isocyanates that can be used is dependent on the molecular weight of the various compounds used and is such that insolubilization does not take place. It is usually preferable to prepare thermoplastic

polyurethanes that are to be used for coatings and inks in an inert solvent such as those described below. The polyurethanes may also be prepared by a one-shot process in which the substituted hydrocarbon diol of formula (I), the multifunctional isocyanate, and optional polyol are combined with or without a catalyst and are allowed to react at room temperature or elevated temperatures to form a thermoplastic polyurethane or a thermoset polyurethane with the thermoplastic or thermoset nature depending on the structure/functionality of the particular ingredients chosen. Such polyurethanes are useful for a variety of end uses including the coating of flexible substrates that are used for fabrics, synthetic leather, as well as other decorative and functional end uses. When prepared in solution form or dissolved in a solvent, the thermoplastic polyurethanes can be prepared in film form by casting the solution onto a release medium such as release paper and removing the solvent by drying.

The choice of a thermoplastic or thermoset polyurethane is dependent on the functionality of the polyols and isocyanates. When difunctional polyols and isocyanates are used thermoplastic polyurethane products will result and when polyols and/or isocyanates of functionality greater than 2 are used polyurethanes with thermoset characteristics will be result.

In an embodiment of this invention, hydroxyl-terminated prepolymers, in which a ratio of two hydrocarbon diol molecules are reacted with one diisocyanate molecule, are reacted with aminoplast resins; illustrative of which are the alkoxymelamines, alkylated benzoquanamines, methylated melamines, butylated melamines, butylated ureas, quanidienes, and the like; in the presence of strong acid catalysts; illustrative of which are para-toluene sulfonic acid, triflic acid, sulfonium salts, and the like; or are reacted with cycloaliphatic epoxides; illustrative of which are 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 6-methyl-3,4-epoxycyclohexylmethyl 6-methyl-3,4-epoxycyclohexanecarboxylate,

bis(3,4-epoxycyclohexylmethyl) adipate, the compounds described in U.S. Patent No. 2,890,194, U.S. Patent No. 2,750,395, U.S. Patent No. 3,318,822, limonene diepoxide and the like; in the presence of triflic acid salts such as ammonium triflate, diethylammonium triflate, diisopropylammonium triflate, sulfonium salts, boron trifluoride salts, and the like.

Although it is not required, it is usually preferred that an inert solvent be used when the reactive polyurethanes of this invention are prepared. Illustrative of such solvents are toluene, methyl ethyl ketone, methyl amyl ketone, methyl i-butyl ketone, xylene, ethoxyethyl acetate, ethoxybutyl acetate, propoxyethyl acetate, dimethylformamide, ethyl acetate, butyl acetate and the like.

Polyurethane foams can be produced from the formula (I) substituted hydrocarbon diols described above and polyfunctional isocyanates and optionally other polyols which are preferentially of tri- or higher functionality. If the formula (I) substituted hydrocarbon diols are used alone to prepare the foams, a trifunctional or higher isocyanate will preferentially be used. Foam formulations are well known to those skilled in the art of polyurethane foam manufacture and, in addition to the formula (I) substituted hydrocarbon diols, such foams are prepared from di- or higher functionality isocyanates, trifunctional polyols, blowing agents, catalysts, surfactants, and other miscellaneous additives as described for example in J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology: Part II. Technology," pp 4-7 (1964) which is incorporated herein by reference. Flexible foams are prepared by either a prepolymer technique, a semi- or quasi-prepolymer technique, or a one-shot method, all of which are described in J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology: Part II. Technology," pp 7-50 (1964) which is incorporated herein by reference. In addition to the formula (I) substituted hydrocarbon diols, other raw materials that may be used in the preparation of rigid foams are well known to those skilled

in the art and are described for example in J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology: Part II. Technology," pp 197-224 (1964) which is incorporated herein by reference. In the case of foams, the blowing agent and surfactant are required items in a formulation unless frothed foams are involved. In this latter instance, a gas such as dry nitrogen or air is whipped or beaten into the liquid ingredients causing a froth to form which is stabilized and reacted to form the foam.

The polyurethane foams of this invention can be used in a variety of end uses as described above, but a particular feature of the foam involves significant oil absorption when significant quantities of the formula (I) substituted hydrocarbon diols are used. Such oil absorption allows the foam to be of eminent use in cleaning up oil spills as can occur when accidents happen during the various means of conveying crude or other oil products. In addition to high absorption, the oil is easily recovered by conveying the foam/oil system through rollers after which the foam can be reused to absorb more oil. Although this property of oil retention will be enhanced when any level of the formula (I) substituted hydrocarbon diols are used, it is preferred that 25 percent or more of the formula (I) substituted hydrocarbon diol be used in the foam manufacture.

In the manufacture of the polyurethanes of this invention, a variety of additives known to those skilled in the art can be used. Illustrative of such additives are pigments, fillers, and colorants; vinyl chloride/vinyl acetate copolymers, phenoxy polymers; silicones, silicone/alkylene oxide copolymers, and fluorochemical surfactants as well as other antiblocking, slip, and flow and leveling agents; and the like. These ingredients can be employed in conventional amounts known in the art.

The polyurethane-containing coatings of this invention can be applied and cured on a variety of substrates known to those skilled in the art of coatings technology. Illustrative of such substrates

are steel, treated steel, tin-plated steel, galvanized steel, treated and untreated aluminum, glass, wood, paper, coated or printed paper, epoxy/fiberglass composites, polymers such as poly(ethylene terephthalate), poly(butylene terephthalate), treated polyethylene and polypropylene, vinyl film, vacuum or vapor deposited aluminum, gold, copper, silver, zinc, nickel, tin, and other metals, electroless nickel, copper-nickel alloys and the like, electrodeposited metals such as silver, copper, nickel, chromium, silver-copper alloys, and the like, glass-reinforced unsaturated-polyester/styrene products, and the like.

Coil coating compositions can be prepared by conventional methods from the polyurethane resins. Illustrative of suitable coil coating compositions include those permissible coil coating compositions which are described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, 1984, the pertinent portions of which are incorporated herein by reference.

Gel coat compositions can be prepared by conventional methods from the polyurethane resins. Conventional gel coat compositions are useful as the exterior paint layer for boats and bathroom fixtures such as shower stalls, bath tub enclosures and the like. A gel coat is a pigmented, filled and prepromoted resin which is sprayed with an initiator onto molds from a high pressure spray gun to a film thickness of up to 0.75 mm. The film cures prior to reinforcement with glass fibers and laminating resins. The gel coat should exhibit low viscosity at high shear, should resist sagging, and have a gel time of about 8-12 minutes. For marine and other applications, the products require hydrolytic stability and good weatherability. Illustrative of suitable gel coat compositions include those permissible gel coat compositions which are described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, 1984, the pertinent portions of which are incorporated herein by reference.

Thermoplastic and thermosetting powder coating compositions can be prepared by conventional methods from

polyurethane resins. The powder coating compositions may be used to coat articles of various shapes and sizes constructed of heat-resistance materials such as glass, ceramic and various metal materials. The powder coating compositions can be especially useful for producing coatings on articles constructed of metals and metal alloys, particularly steel articles. Examples of formulation methods, additives, and methods of powder coating application may be found in User's Guide to Powder Coating, 2nd Ed., Emery Miller, editor, Society of Manufacturing Engineers, Dearborn, (1987). See also, for example, World Patent No. WO 06564, the disclosure of which is incorporated herein by reference. Illustrative of suitable powder coating compositions include those permissible powder coating compositions which are described in Kirk-Othmer, Encyclopedia of Chemical Technology, Third Edition, 1984, the pertinent portions of which are incorporated herein by reference.

As used herein, the term "polyol" is contemplated to include all permissible hydrocarbon compounds having 2 or more hydroxyl groups, e.g., diols, triols and the like.

As used herein, the term "ester-diol" is contemplated to include all permissible ester-diols formed from the Tischenko reaction of substituted hydroxyaldehydes during the processes of this invention. For example, 2-methyl-2-hydroxymethylbutyl 2-methyl-2-hydroxymethylbutyrate may be formed from the Tischenko reaction of 2-ethyl-2-methyl-3-hydroxyaldehyde during the processes of this invention.

For purposes of this invention, the term "hydrocarbon" is contemplated to include all permissible compounds having at least one hydrogen and one carbon atom. In a broad aspect, the permissible hydrocarbons include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic organic compounds which can be substituted or unsubstituted.

As used herein, the term "substituted" is contemplated to include all permissible substituents of hydrocarbon compounds unless otherwise indicated. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and nonaromatic substituents of hydrocarbon compounds. Illustrative substituents include, for example, alkyl, alkyloxy, aryl, aryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or more, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate hydrocarbon compounds. This invention is not intended to be limited in any manner by the permissible substituents of hydrocarbon compounds.

Certain of the following examples are provided to further illustrate this invention.

<u>Glossary of Terms</u>

Crosshatch Adhesion - Procedure conducted in accordance with ASTM D 3359-87.

Pencil Hardness - Procedure conducted in accordance with ASTM D 3363-74.

Specular Gloss (20°) - Procedure conducted in accordance with ASTM D 523-78.

Specular Gloss (60°) - Procedure conducted in accordance with ASTM D 523-78.

Cured Film Thickness - Procedure conducted in accordance with ASTM D 523-78.

Impact Resistance (Forward) - Procedure conducted in accordance with ASTM D 2794-84.

Impact Resistance (Reverse) - Procedure conducted in accordance with ASTM D 2794-84.

Double Rubs - Solvent resistance was measured as the number of solvent (methyl ethyl ketone) double rubs that were

required to cut through the coating. If 300 rubs or more did not cut through the coating, the coating was recorded as >300. To perform the test, the solvent-soaked cloth was rubbed back and forth with hand pressure. A rub back and forth was designated as one "double rub."

Acid Etch Resistance - A Fini automatic transfer pipette was used to place a series of 50 micro-liter droplets of 15% sulfuric acid solution at approximately 1/4-inch intervals in two rows along the length of one or more coated panels. Usually two panels were required to provide the length of surface needed to examine the temperature range of 40°C to 100°C that is achieved in the gradient temperature oven. Two rows of spots are used for duplication of the test. The coated panels are placed in an end-to-end position on the heating bank of a BYK Chemie gradient temperature oven. The first spots are aligned with the #1 rod which is at 40°C. This results in the various spots being at temperatures that range to 100°C. The sulfuric acid solution droplets are allowed to contact the coating for various times at the indicated temperatures. After the desired heating time, the panels are removed from the gradient oven, cooled to room temperature, rinsed thoroughly with distilled water, lightly patted dry, and evaluated.

Evaluation consists of examining the areas that had been covered with the droplets with a 10-power, lighted magnifier. The following are points of comparison observed and recorded for each coating.

a) The lowest temperature spot area with a visible defect in the coating. A "visible defect" is the first sign of any blush, bubbling, yellowing, or other visible change.

b) The lowest temperature spot with a severe defect. A "several defect" is blistering or complete removal of the coating with the substrate visible. This latter factor means the acidic solution has cut through the coating to the substrate.

Catalyst I - A 40 percent solution of p-toluenesulfonic acid in methanol.

Catalyst II - A solution of butyl stannoic acid commercially available from Atochem North America as Fascat®4100.

Melamine I - A polymethoxymethyl melamine commercially available from American Cyanamid as Cymel® 303.

Surfactant I - A 25 percent solution of a methoxy-terminated poly(ethylene oxide) modified polydimethylsiloxane in methyl amyl ketone commercially available from OSi Specialties Inc. as Silwet® L-77.

Surfactant II - A 25 percent solution of a methoxy-terminated ethylene oxide/propylene oxide copolymer modified polydimethylsiloxane in methyl amyl ketone commercially available from OSi Specialties Inc. as Silwet® L-7001.

Polymeric Isocyanate I - An aliphatic polyisocyanate commercially available from Bayer as Desmodur® N-3300.

## Examples

### Example 1

75.5 grams of cyclohexane and 10.1 grams of a catalyst powder (35-45% chromium oxide, 35-45% copper oxide, 1-5% manganese oxide) available from United Catalysts Inc. as United Catalyst G-89 were charged to a 600 milliliter Parr reactor. The reactor was heated to 220°C and rapidly stirred. The reactor was pressurized to 600 psig hydrogen. As hydrogen was consumed, the reactor was periodically re-pressurized to 600 psig. The process reduced the manganese promoted copper-chromite catalyst to the active copper-chromate hydrogenation catalyst. The activation process required 2 hours.

Once the catalyst was activated, the reactor was cooled to 60°C and 200 grams of a crude 2-ethyl-2-methyl-3-hydroxypropanal mixture was charged. The crude 2-ethyl-2-methyl-3-hydroxypropanal mixture was 0.03 % methanol, 0.9 % 2-methybutyraldehyde, 1.0 % triethylamine, 0.08 % 2-methylbutanol, 81.0 % 2-ethyl-2-methyl-3-

hydroxypropanal, 4.3 % 2-ethyl-2-methyl-1,3-propanediol and 10.2 % ester-diol. The reactor was heated to 120°C and pressurized to 700 psig hydrogen. The reaction solution was rapidly stirred. As hydrogen was consumed the reactor was re-pressurized to 700 psig hydrogen (typically when the reactor pressure dropped below 500 psig). Reaction solution samples were taken every 30 minutes. The reaction was complete in 1.5 hours. The 1.5 hour reaction sample analyzed as 2.2 % methanol, 0.04 % 2-methylbutyraldehyde, 0.9 % triethylamine, 0.5 % 2-methylbutanol, 0.14 % 2-ethyl-2-methyl-3-hydroxypropanal, 81.4 % 2-ethyl-2-methyl-1,3-propanediol, and 13.0 % ester-diol. These results correspond to a hydroxyaldehyde conversion of >99% and a 2-ethyl-2-methyl-1,3-propanediol selectivity of 94 %. The above experimental results translate to an average rate of 0.087 moles/gram catalyst/hour.

## Polyurethanes

Hydroxyl capped polyurethanes were prepared by the reaction of 2-ethyl-2-methyl-1,3-propanediol and neopentyl glycol with either isophorone diisocyanate (Examples 2 and 3) or hexamethylene diisocyanate (Examples 6 and 7), in the presence of 0.02 % of dibutyltin dilaurate catalyst with a hydroxyl to isocyanate ratio was 2:1.

Coatings were prepared by reacting these polyurethanes with either polyfunctional isocyanates (Examples 4, 5, 8 and 9) or aminoplast crosslinking agents (Examples 10, 11, 12 and 13). Improved coating hardness (measured by Pencil Hardness) and better acid etch resistance were observed for the 2-ethyl-2-methyl-1,3-propanediol based polyurethanes.

## Example 2

59.68 grams (0.5 moles) of 2-ethyl-2-methyl-1,3-propanediol, 0.0296 grams (0.025%) of dibutyltin dilaurate and 16.2

grams of n-methyl-2-pyrrolidone were charged to a 500 milliliter, 4-necked flask equipped with a mechanical stirrer, nitrogen sparger, inlet and outlet nitrogen connection which also functioned as a feeding port, and thermometer. While sparging with nitrogen and stirring, these ingredients were heated to 80°C and held at this temperature for 1 hour to remove water. The temperature was then decreased to 55°C and 56.68 grams (0.25 moles) of isophorone diisocyanate were slowly added dropwise to the reaction mass. When addition was complete, the reaction was allowed to proceed at 55°C for three hours, and then the reaction mass was allowed to cool to room temperature. The resulting polyurethane had a hydroxyl number of 237. Molecular weight determination by gel permeation chromatography using a polystyrene standard resulted in an apparent number average molecular weight of 591, a weight-average molecular weight of 694, and a polydispersity of 1.17.

Example 3

A polyurethane was prepared in the same manner as that of Example 2 except the following ingredients were used: 52.59 grams (0.5 mole) of 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 56.68 grams (0.25 mole) of isophorone diisocyanate, 25.6 grams of n-methyl-2-pyrrolidone, and 0.0278 grams (0.025 weight percent) dibutyltin dilaurate catalyst. The resulting polyurethane had a hydroxyl number of 259. Molecular weight determination by gel permeation chromatography using a polystyrene standard resulted in an apparent number average molecular weight of 834, a weight-average molecular weight of 904, and a polydispersity of 1.08.

Examples 4 and 5

These examples describe the preparation of thermally curable coatings prepared from the polyurethanes of Examples 2 and 3, an isocyanate crosslinking agent and other ingredients listed in Table

A below. After thorough mixing of the ingredients, the resulting mixtures were coated onto phosphatized steel panels with a No. 20 wire-wound rod and cured at 100°C for 30 minutes. Hard clear coatings resulted. The coatings were then tested by the indicated tests with the results given in Table A.

Table A

| Ingredients, grams | Example 4 | Example 5 |
|---|---|---|
| Example 2 Polyurethane | 10.0 | ---- |
| Example 3 Polyurethane | ---- | 9.4 |
| Polymeric Isocyanate I | 9.69 | 9.69 |
| Catalyst II | 0.03 | 0.03 |
| 2,4-Pentanedione | 0.03 | 0.03 |
| Ethyl EthoxyPropionate | 11.0 | 11.0 |
| Cured Film Properties | | |
| Cured Film Thickness, mils | 1.9 | 2.0 |
| Specular Gloss (20°) | 85.0 | 84.8 |
| Specular Gloss (60°) | 94.2 | 94.1 |
| Pencil Hardness | 4H | 3H |
| Impact Resistance | | |
| Forward, in-lbs. | 300+ | 300+ |
| Reverse, in-lbs. | 300+ | 300+ |
| Acid Etch Resistance (°C) (1st visible/1st severe) | 68/77 | 68/77 |
| Crosshatch Adhesion | 5B | 5B |
| Double Rubs | 110 | 100 |

Example 6

59.68 grams (0.5 moles) of 2-ethyl-2-methyl-1,3-propanediol, 0.0261grams (0.025%) of dibutyltin dilaurate catalyst and 14.5 grams of n-methyl-2-pyrrolidone were charged to a 500 milliliter, 4-necked flask equipped with a mechanical stirrer, nitrogen sparger, inlet and outlet nitrogen connection which also functioned as a feeding port, and thermometer. While sparging with nitrogen and stirring, these ingredients were heated to 80°C and held at this temperature for one hour to remove water. The temperature was then decreased to 55°C and 42.89 grams (0.25 moles) of hexamethylene diisocyanate were slowly added to the reaction mass. When addition was complete, the reaction was allowed to proceed at 55°C for three hours, and then the reaction mass was allowed to cool to room temperature. The resulting polyurethane had a hydroxyl number of 291. Molecular weight determination by gel permeation chromatography using a polystyrene standard resulted in an apparent number average molecular weight of 484, a weight-average molecular weight of 516, and a polydispersity of 1.07.

Example 7

A polyurethane was prepared in the same manner as that of Example 6 except the following ingredients were used: 52.59 grams (0.5 mole) of 2,2-dimethyl-1,3-propanediol (neopentyl glycol), 42.89 grams (0.25 mole) of an hexamethylene diisocyanate, 13.5 grams of n-methyl-2-pyrrolidone, and 0.0243 grams (0.025 weight percent) dibutyltin dilaurate catalyst. The resulting polyurethane had a hydroxyl number of 313. Molecular weight determination by gel permeation chromatography using a polystyrene standard resulted in an apparent number average molecular weight of 487, a weight-average molecular weight of 527, and a polydispersity of 1.08.

Examples 8 and 9

These examples describe the preparation of thermally curable coatings prepared from the polyurethanes of Examples 6 and 7, an isocyanate crosslinking agent and other ingredients listed in Table B below. After thorough mixing of the ingredients, the resulting mixtures were coated onto phosphatized steel panels with a No. 20 wire-wound rod and cured at 90°C for 30 minutes. Hard clear coatings resulted. The coatings were then tested by the indicated tests with the results given in Table B.

Table B

| Ingredients, grams | Example 8 | Example 9 |
|---|---|---|
| Example 6 Polyurethane | 10.0 | ---- |
| Example 7 Polyurethane | ---- | 9.4 |
| Polymeric Isocyanate I | 9.69 | 9.69 |
| Catalyst II | 0.03 | 0.03 |
| 2,4-Pentanedione | 0.03 | 0.03 |
| Ethyl EthoxyPropionate | 11.0 | 11.0 |
| Cured Film Properties | | |
| Cured Film Thickness, mils | 1.8 | 1.8 |
| Specular Gloss (20°) | 83.4 | 82.4 |
| Specular Gloss (60°) | 93.5 | 93.2 |
| Pencil Hardness | 4H | H |
| Impact Resistance | | |
| Forward, in-lbs. | 300+ | 300+ |
| Reverse, in-lbs. | 300+ | 300+ |
| Acid Etch Resistance (°C) (1st visible/1st severe) | 66/77 | 64/74 |

| | | |
|---|---|---|
| Crosshatch Adhesion | 5B | 5B |
| Double Rubs | 120 | 120 |

Examples 10-13

The polyurethane polymers of Examples 2, 3, 6 and 7 were formulated in a 3 to 1 ratio by weight with Melamine I crosslinking agent. To each of these mixtures, 0.5% by weight of Catalyst I, 0.5% by weight of Surfactant I, and 0.5% by weight of Surfactant II were added and then well mixed. The resultant liquid coating formulations were applied to steel panels with a wire-wound draw-down rod and baked for 30 minutes in a 140°C oven. The resulting coatings had the properties set out in Table C below:

Table C

| Example # | 10 | 11 | 12 | 13 |
|---|---|---|---|---|
| Polymer Prepared in Example # | 2 | 3 | 6 | 7 |
| Pencil Hardness | 4H | 4H | 4H | 2H |
| Impact Resistance (Forward/Reverse) | 40/<5 | 35/<5 | 30/<5 | 30/<5 |
| Specular Gloss (20°/60°) | 82.7/94.5 | 71.5/92.1 | 84.1/95.4 | 83.1/94.7 |
| Acid Etch Resistance (°C) | 68/71 | 66/70 | 62/65 | 59/61 |

(1st visible/1st severe)

| | | | | |
|---|---|---|---|---|
| Double Rubs | >300 | >300 | >300 | >300 |

Examples 14 and 15

Polyurethane reactions were conducted in the same manner as that of Examples 2 and 3 except no solvent was used for the reaction. The resulting polyurethane for Example 14 had an hydroxyl number of 261. Molecular weight determination by gel permeation chromatography using a polystyrene standard resulted in an apparent number average molecular weight of 331, a weight-average molecular weight of 392, and a polydispersity of 1.19. For Example 15, neopentyl glycol remained solid at the reaction temperature, therefore, no product was produced.

Example 16

This example describes the preparation of a thermally curable coating prepared from the polyurethane of Example 14. A polyurethane coating was prepared following the procedure in Example 4. After thorough mixing of the ingredients, the resulting mixtures were coated onto phosphatized steel panels with a No. 20 wire-wound rod and cured at 90°C for 45 minutes. The coating was examined and found to be smooth and clear. The resulting coating had a B Pencil Hardness, a 5B Crosshatch Adhesion, a Specular Gloss (20°C/60°C) of 83.8/93.9, an Impact Resistance (forward/reverse) of 300+/295 in-lbs, and an Acid Etch Resistance (1st visible/1st severe) of 68/76. Solvent resistance was found to be 70 double rubs.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

Claims

1. A polyurethane comprising the reaction product of (i) a substituted hydrocarbon diol comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms, and/or a derivative of said substituted hydrocarbon diol, and (ii) a polyfunctional isocyanate.

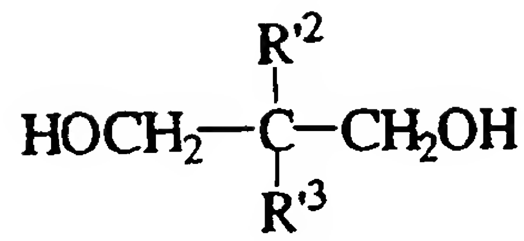
2. The polyurethane of claim 1 further comprising a polyol different from said substituted hydrocarbon diol or derivative thereof.

3. The polyurethane of claim 1 wherein the substituted hydrocarbon diol is represented by the formula:

$$HO - R'^{1} - OH$$

wherein $R'^{1}$ is a substituted hydrocarbon residue having 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms.

4. The polyurethane of claim 1 wherein the substituted hydrocarbon diol is represented by the formula:



wherein R'2 and R'3 are the same or different and are linear or branched alkyl having from 1 to 4 carbon atoms.

5. The polyurethane of claim 1 in which the substituted hydrocarbon diol is selected from 2-ethyl-2-methyl-1,3-propanediol, 2,2-dimethyl-1,3-propanediol, 3-ethyl-2-methyl-1,3-propanediol, 2-ethyl-3-propyl-1,3-propanediol, 2,3-dimethyl-3-ethyl-1,3-propanediol, 2-ethyl-3-methyl-3-propyl-1,3-propanediol, 2,3-diethyl-3-methyl-1,3-propanediol, 3-ethyl-2,2,3-trimethyl-1,3-propanediol, 2,2-dimethyl-3-ethyl-3-propyl-1,3-propanediol, 2-methyl-2-propyl-1,3-propanediol, 2,3-dimethyl-3-ethyl-2-propyl-1,3-propanediol, 2,3-dipropyl-3-ethyl-2-methyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-butyl-2,3-diethyl-3-methyl-1,3-propanediol, 2-butyl-2,3-diethyl-3-propyl-1,3-propanediol, 3-butyl-2-propyl-1,3-propanediol, and mixtures thereof.

6. The polyurethane of claim 1 in which the substituted hydrocarbon diol is 2-ethyl-2-methyl-1,3-propanediol.

7. The polyurethane of claim 1 wherein the derivative of said substituted hydrocarbon diol is selected from polyesters, silicone-containing compounds, polyols initiated with said substituted hydrocarbon diols, and mixtures thereof.

8. The polyurethane of claim 1 in which the polyfunctional isocyanate is selected from 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenylmethane diisocyanate (MDI), 4,4'-dicyclohexyldiisocyanate, meta- and para-tetramethyl xylene

diisocyanate, 3-isocyanatomethyl-3,5,5,-trimethylcyclohexylisocyanate, hexamethylene diisocyanate, 2,2,4- and 2,4,4-trimethylenehexamethylene diisocyanate, meta- and para-phenylene diisocyanate, isophorone diisocyanate, 2,4-, 2,6- and 2,4-/2,6-bromotoluene diisocyanate, 4-bromo-meta-phenylene diisocyanate, ortho- and meta-trifluoromethylphenylisocyanate; ortho, meta-, and para-fluorophenylisocyanate; 4,6-dibromo-meta-phenylene diisocyanate; ortho-, meta-, and para-chlorophenyl isocyanate, 4,4',4"-triisocyanatotriphenylmethane, and mixtures thereof.

9. The polyurethane of claim 2 wherein said polyol is selected from a poly(tetramethylene oxide) polyol, a polylactone polyol, a polycarbonate polyol, a poly(alkylene oxide) polyol, a polyester polyol, a polyether polyol, and mixtures thereof.

10. A process for preparing a polyurethane which comprises reacting a substituted hydrocarbon diol comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms, and/or a derivative of said substituted hydrocarbon diol, with a polyfunctional isocyanate to form said polyurethane.

11. A process for preparing a polyurethane which comprises: (1) subjecting a first reaction mixture comprising a substituted hydroxyaldehyde to hydrogenation in the presence of a hydrogenation catalyst to produce a second reaction mixture comprising a substituted hydrocarbon diol comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly

arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms; and (2) reacting said substituted hydrocarbon diol with a polyfunctional isocyanate to form said polyurethane.

12. A process for preparing a polyurethane which comprises: (1) reacting an olefinically unsaturated compound with carbon monoxide and hydrogen in the presence of a metal-ligand complex catalyst to produce a first reaction mixture comprising a substituted first aldehyde; (2) subjecting said first reaction mixture and a substituted or unsubstituted second aldehyde to aldol condensation in the presence of an aldol condensation catalyst to produce a second reaction mixture comprising a substituted hydroxyaldehyde; (3) subjecting said second reaction mixture to hydrogenation in the presence of a hydrogenation catalyst to produce a third reaction mixture comprising a substituted hydrocarbon diol comprised of primary hydroxyl groups and 5 or more carbon atoms in which the primary hydroxyl groups are separated by 3 or more carbon atoms linearly arranged and in which at least one of said carbon atoms linearly arranged is a disubstituted carbon atom or at least 2 of said carbon atoms linearly arranged are monosubstituted carbon atoms; and (4) reacting said substituted hydrocarbon diol with with a polyfunctional isocyanate to form said polyurethane.

13. A two-package polyurethane system comprising (i) a first package comprised of a polyurethane of claim 1, and (ii) a second package comprised of a polyol.

14. A polyurethane foam comprised of the polyurethane of claim 1, a blowing agent and a surfactant.

15. A curable coating composition comprising the polyurethane of claim 1.

16. A cured film prepared from the coating composition of claim 16.

17. The curable coating composition of claim 15 which is cured with moisture or thermal energy or a mixture thereof.

18. An adhesive composition, an ink composition, a sealant composition, a coil coating composition, a gel coat composition or a powder coating composition comprising the polyurethane of claim 1.

# INTERNATIONAL SEARCH REPORT

Int' ational application No.
PCT/US 96/17884

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08G 18/32, C09D 175/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08G, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X | EP, A1, 0455291 (AKZO N.V.), 6 November 1991 (06.11.91), page 7, line 26, claims 1,12, abstract<br>-- | 1-18 |
| X | EP, A1, 0530806 (MITSUBISHI KASEI CORPORATION), 10 March 1993 (10.03.93), page 2, line 22 - line 55, abstract<br>-- | 1-18 |

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 17 February 1997 | 26.03.97 |
| Name and mailing address of the ISA/<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL-2280 HV Rijswijk<br>Tel. ( + 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: ( + 31-70) 340-3016 | Authorized officer<br>JACK HEDLUND |

# INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 96/17884

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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SA 146673

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03/02/97

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